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THE SPECIFIC HEATS OF SOME METALLIC ELEMENTS

Part IV. The Residual Spectrum

By Sir C. V. Raman

(*Memoir No. 93 from the Raman Research Institute, Bangalore 6*)

Received February 25, 1957

1. Introduction

The theory of the specific heats of crystals developed in a recent paper by the present author is based on the result that the structure of a crystal containing p atoms in each unit cell has $(24p - 3)$ normal modes of vibration characterised by sharply defined monochromatic frequencies. These may be described as the modes of internal vibration of the groups of $8p$ atoms each included in volume elements of the crystal whose dimensions are twice as large in each direction as those of the unit cell. The three degrees of freedom of atomic movement left out in this description represent the three translations of each group of $8p$ atoms. The vibration spectrum resulting from these translations may be designated as " the residual spectrum " and its nature was discussed in the paper already cited. The contribution to the thermal energy of the crystal arising from the translations of each group of $8p$ atoms is represented by an integral in which Einstein's expression for the average energy of an oscillator of frequency ν appears multiplied by a quantity $9.\nu^2 d\nu/\nu_1^3$ and the product is integrated between the limits 0 and ν_1. The upper limit is the upper limit of frequency in the residual spectrum and is also the lowest of the $(24p - 3)$ frequencies characteristic of the structure.

In the case of the metallic elements now under consideration, $p = 1$ and the residual spectrum thus represents only 3 out of every 24 degrees of atomic freedom of movement. It nevertheless plays a major role in determining the magnitude of the specific heat of the metals at very low temperatures. Hence, a comparison of the experimental data at such low temperatures with the calculated values is of importance for establishing the correctness of the present approach to the theory of their specific heats. It is the object of the present paper to present the results of such a comparison.

As the determinations by Giaque and his collaborators which have so far been the basis of our discussion stop at 15° K., we have necessarily to make use of the results reported by other investigators for still lower temperatures. The circumstance that the specific heats at such temperatures are very low and increase rapidly with rise of temperature sets a limit to the

possible accuracy of their experimental determinations. The specific heat also varies enormously from metal to metal and hence even a small percentage of impurity would affect the determined values, raising them or lowering them, as the case may be. These factors may be responsible for the divergences noticed between the results reported by Giaque and collaborators and those obtained by other investigators in the temperature ranges common to them. These divergences are particularly large in the case of aluminium which has a very low specific heat in the range 0 to 15° K. but are less serious in the case of the other three metals, copper, silver and lead.

2. THE ELECTRONIC SPECIFIC HEATS

The observed variation of the specific heats of metals with temperature in the vicinity of the absolute zero differs in its features from that observed in the case of insulators, *e.g.*, diamond or the alkali halides. The curves do not touch the axis of the abscissæ but meet it at the origin making a definite angle with it. The specific heats in this region can be represented by an expression of the form $AT + BT^3$. These facts are explained on the basis that the first term represents the contribution arising from the thermal agitation of the electrons and the second from the thermal agitation of the atoms themselves. This interpretation finds support in the fact that in the case of metals exhibiting superconductivity, *e.g.*, aluminium and lead, the coefficient A exhibits a distinctly larger value in the range of superconductivity, while the coefficient B remains unaltered.

TABLE I

Specific Heats at Low Temperatures

$c_v = AT + BT^3$

Substance	Range of measurement	$A \times 10^4$	$B \times 10^5$	Author
Aluminium ..	0–20° K.	3·48	0·63	Kok & Keesom
	0– 4° K.	3·42	0·68	Howling *et al.*
Copper ..	0–20° K.	1·78	1·24	Kok & Keesom
	0– 5° K.	1·64	1·14	Corak *et al.*
Silver ..	0– 5° K.	1·46	4·06	Corak *et al.*
Lead ..	0– 5° K.	7·48	52·04	Horowitz *et al.*

Table I shows the results for the four metals now under consideration reported by various authors. It will be seen that the coefficient A is largest for lead; aluminium stands next and is followed by copper and silver, the coefficients for the latter not being very different. The value quoted in the case of lead is for the state of the metal in which the superconductivity has been eliminated by a strong magnetic field.

It follows from what has been stated above that for a comparison of the experimental data with the results of the present theory, it is necessary to add to the specific heat a term representing the electronic contribution. This has been done, making use of the results of the authors quoted in the table. We shall discuss first the results thus obtained in the case of copper, silver and lead, since in the cases of these metals the determinations which we make use of are in reasonable agreement with those reported by Giaque and collaborators. The case of aluminium where this is not the case will also be discussed.

3. Comparison of Theory and Experiment

Copper.—The specific heat of copper in the range between 0° and 20° K. has been reported by Kok and Keesom, while in the more limited range

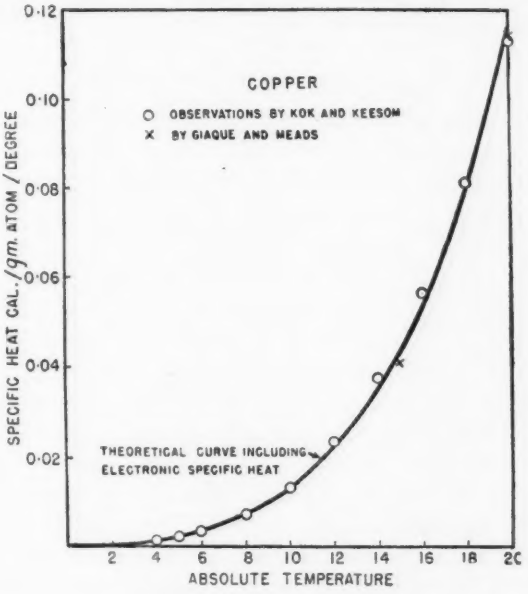

Fig. 1. Specific Heats of Copper.

from 0 to 5° K., measurements have been made by Corak, Garfunkel, Satterthwaite and Wexler. We present the comparison between theory and experiment in the form of two graphs, one in the range 0 to 20° K. and the other in the range 0 to 5° K. In the latter range the results of Kok and Keesom are systematically in excess of those reported by Corak *et al.*, the difference being about 8% at 5° K. However, a satisfactory overall agreement between theory and experiment is exhibited by both the graphs.

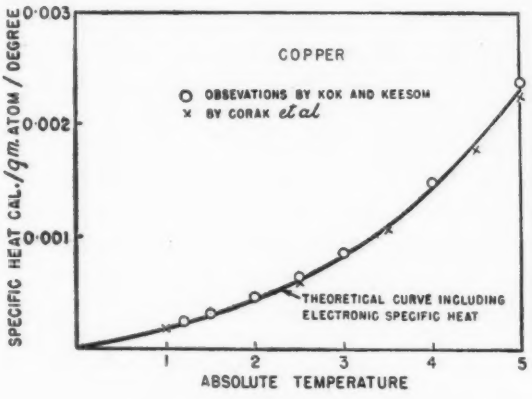

FIG. 2. Specific Heats of Copper.

Silver.—Likewise in the case of silver we present the results in the form of two graphs, Figs. 3 and 4 respectively. Here again, a satisfactory agreement emerges between the theoretical results and the experimental data.

Lead.—All the four characteristic frequencies besides the residual spectrum contribute to the observed specific heat at 20° K. and this continues to be the case upto 10° K. At still lower temperatures the contributions of only the lowest of the four characteristic frequencies and the residual spectrum predominate. Below 5° K., only the residual spectrum is of importance. As in the previous cases we present a comparison between theory and experiment in the form of two graphs covering the ranges 0 to 20° K. and 0 to 5° K. as Figs. 5 and 6 respectively. In Fig. 5 the available determinations of various authors have all been plotted and it will be seen that between 15° and 20° K. the determinations agree generally with each other and with the course of the theoretical curve. Between 5° and 15° K. the only observations are those by Keesom and Van den Ende whose results appear to be rather erratic but nevertheless follow the trend of the theoretical curve fairly well. At the lowest temperatures the results of these same authors are notice-

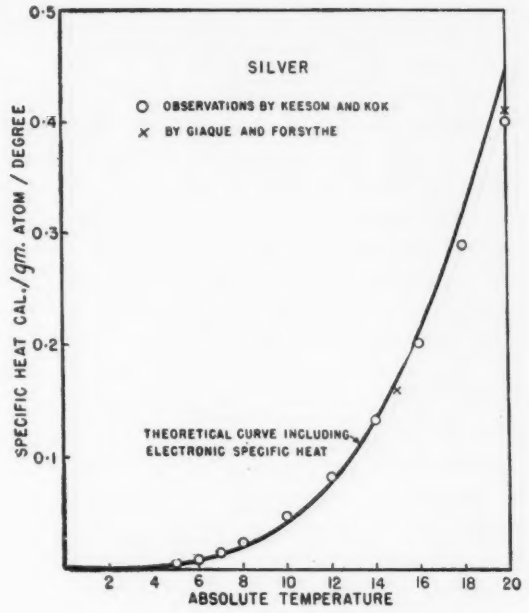

FIG. 3. Specific Heats of Silver.

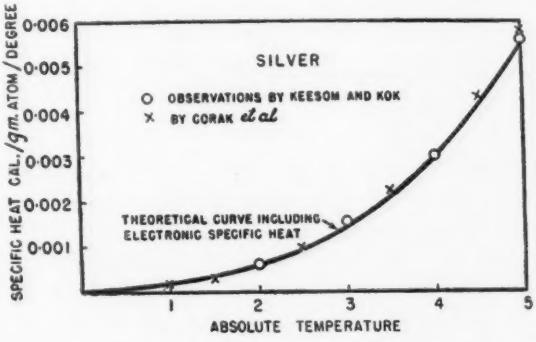

FIG. 4. Specific Heats of Silver.

ably in excess of those deduced from theory. But as will be seen from Fig. 6 the observations by Horowitz *et al*, are in excellent accord with the calculated values.

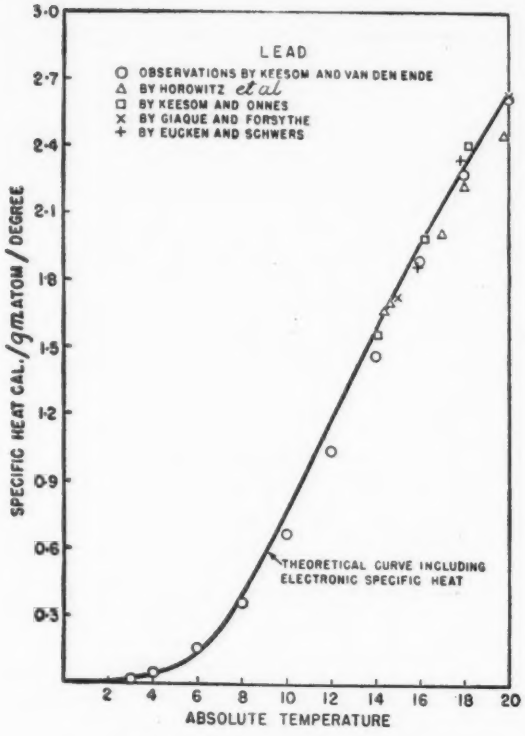

FIG. 5. Specific Heats of Lead.

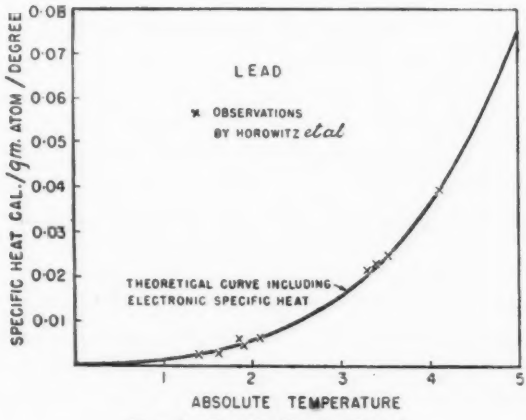

FIG. 6. Specific Heats of Lead.

Aluminium.—Of the four metals studied, aluminium has the lowest specific heats in the range 0 to 20° K., and the electronic contribution forms an important part of the whole. Making use of the characteristic frequencies deduced in Part III from the specific heat data themselves as reported by Giaque and Meads and taking into account the electronic contribution, the specific heat curve has been computed. The graph thus obtained coincides with the observations reported by Kok and Keesom only at the lowest temperatures where the electronic heat contribution predominates. In the range from 5 to 20° K., the data reported by Kok and Keesom deviate progressively from the theoretical curve, the observed values being everywhere in excess by quantities ranging from 8 to 20% of the calculated ones. They are also in excess of the values reported by Giaque and Meads for 15° and 20° K. to a similar extent.

Throughout the range now under discussion the specific heat of aluminium is determined solely by the contribution of the residual spectrum with the addition of the electronic specific heat. The values reported by Kok and Keesom throughout the range would be in fair agreement with the theoretical calculations if the upper limit of frequency in the residual spectrum were taken as 146 $cm.^{-1}$ which is nearly the value deduced in Part II by an approximate method instead of as 160 $cm.^{-1}$ calculated in Part III from the specific heat data themselves. But the former assumption would result in the theoretically calculated values at higher temperatures differing from those reported by Giaque and Meads by more than the probable magnitude of their experimental errors. Considering these facts, it appears correct to assume that the values reported by Kok and Keesom for aluminium in the upper part of the temperature range between 0 to 20° K. are in excess of the real values by quantities of the order of 10%.

Summary

The theoretical calculation of the specific heats of the four metals aluminium, copper, silver and lead which in Part III were shown to be in satisfactory accord with the experimental data reported by Giaque and collaborators in the range from 15 to 300° K. have in the present paper been extended down to the absolute zero. When the contribution arising from the thermal agitation from the electrons is included, the calculated specific heats are in satisfactory accord with the results reported by various investigators on the low temperature specific heats of these metals. The agreement is excellent in the cases of copper, silver and lead, but not so satisfactory for aluminium, the available data for which are meagre and appear to be of doubtful accuracy.

REFERENCES

1. Giaque and Meads .. *J. Am. Chem. Soc.*, 1941, **63**, 1897.
2. —— and Forsythe .. *Ibid.*, 1941, **63**, 1902.
3. Kok and Keesom .. *Physica*, 1936, **3**, 1035 (Al, Cu).
4. Corak and others .. *Physical Review*, 1955, **98**, 1699 (Cu, Ag).
5. Horowitz and others .. *Ibid.*, 1952, **88**, 1182 (Pb).
6. Howling and others .. *Proc. Roy. Soc.* (London), 1955, **229 A**, 86 (Al).
7. Keesom and Kok .. *Communications Univ. Leiden*, 1932, No. 219 (*d*) and 1933, No. 232 (*d*), (Cu & Ag).
8. Keesom and Van den Ende *Ibid.*, 1930, No. 203 (*d*), and 1931, No. 213 (*c*), (Pb).
9. —— and Onnes. Eucken and Schwers *Landolt Bornstein Tabellen Hauptwerk* (5 Auflage, 2 Band), p. 1242 (Pb).

THE OPTICAL ROTATORY DISPERSION OF QUARTZ

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Abstract

Many formulæ have been proposed to express numerically the rapid increase of the rotatory power of quartz with decrease of wavelength. An examination of these formulæ shows that they are wholly inappropriate for the case of quartz. It has been shown that the entire range of data from the visible to the extreme ultraviolet is accurately represented by a new type of formula involving only two constants, *viz.*,

$$\rho = \frac{k\lambda^2}{(\lambda^2 - \lambda_0^2)^2},$$

where $k = 7{\cdot}19$ and $\lambda_0 = 0{\cdot}0926283\,\mu$. A theoretical interpretation of the new formula has been given on the basis of a simple coupled oscillator model.

Introduction

The phenomenon of optical activity was discovered in the year 1811 by Arago in pieces of quartz cut perpendicular to the optic axis. Soon afterwards, Biot showed that the rotatory power in the visible region of the spectrum varies inversely as the square of the wavelength, *i.e.*, $\rho = k/\lambda^2$. The rotatory dispersion of quartz has subsequently been the subject of extensive experimental study. This has been reviewed by Sosman in his book on the properties of silica (1927) and by Lowry in his treatise on optical rotatory power (1935). More recently, measurements have been pursued into the remote ultraviolet upto 1500 Å by Servant (1939). It is evident from these determinations that Biot's Law fails completely as we move away from the visible spectrum. Indeed, from 6000 Å to 1500 Å the rotatory power increases by nearly 40 times instead of 16 times as required by the inverse square formula.

There have been several attempts in the past at expressing the rotatory dispersion in terms of assumed characteristic frequencies. In the present

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paper, these formulæ have been examined and it is shown that they are completely unsatisfactory for the case of quartz. A new type of formula has been suggested, a single term of which fits the whole range of data from the visible to the extreme ultraviolet very accurately. On the basis of a simple coupled oscillator model, a theoretical interpretation has been given to this formula. It is proved that the new formula is not open to the same theoretical objection which disqualifies all the earlier formulæ, which are principally of the Drude type.

EARLIER FORMULÆ FOR THE ROTATORY DISPERSION OF QUARTZ

The first attempt at a theoretical formula for the rotatory dispersion of quartz was made by Drude in his *Lehrbuch der Optik* (1900), where he proposed the form

$$\rho = \sum_r \frac{Q_r}{\lambda^2 - \lambda_r^2}, \tag{1}$$

where ρ is the rotatory power in degrees per millimetre, Q_r is a constant corresponding to the characteristic absorption wavelength λ_r in microns, the summation being performed over all the r absorption frequencies. Drude found that the then available data could be fitted by a two term formula, where

$$Q_1 = 12{\cdot}2, \qquad Q_2 = -5{\cdot}046,$$
$$\lambda_1^2 = 0{\cdot}010627, \qquad \lambda_2^2 = 0,$$

the negative term being unambiguously indicated to be necessary.

Lowry (1912) found that Drude's formula is not accurate enough to fit his first series of extended measurements and hence altered it to

$$\rho = \frac{11{\cdot}6064}{\lambda^2 - 0{\cdot}010627} - \frac{4{\cdot}3685}{\lambda^2} + \frac{13{\cdot}42}{\lambda^2 - 78{\cdot}22}, \tag{2}$$

the additional third term corresponding to the infrared absorption band. The later and more accurate readings of Lowry and Coode-Adams (1927) required a further modification of (2), and their final formula is

$$\rho = \frac{9{\cdot}5639}{\lambda^2 - 0{\cdot}0127493} - \frac{2{\cdot}3113}{\lambda^2 - 0{\cdot}000974} - 0{\cdot}1905, \tag{3}$$

where, instead of the single absorption band at 1031 Å used in the previous formulæ, two new characteristic wavelengths at 1129 Å and 312 Å have been used, the effect of the infrared being substituted by a constant.

However, all these formulæ fail to represent the measurements of Duclaux and Jeantet (1926) extending up to 1854 Å. These authors have proposed the formula

$$\rho = \frac{7{\cdot}284}{\lambda^2 - 0{\cdot}015114} \tag{4}$$

to approximately fit their data. But, as the discrepancy with this simple formula is quite considerable even in the near ultraviolet, another was worked out by Bradshaw and Livens (1929), *viz.*,

$$\rho = \frac{845{\cdot}694}{(\lambda^2 - 0{\cdot}01274912)} - \frac{0{\cdot}40235}{(\lambda^2 - 0{\cdot}01274912)^2} - \frac{838{\cdot}4320}{(\lambda^2 - 0{\cdot}0120800)} - \frac{0{\cdot}1331233}{(\lambda^2 - 0{\cdot}0120800)^2} + \frac{43{\cdot}05794}{(\lambda^2 - 80{\cdot}00)} + \frac{2119{\cdot}117}{(\lambda^2 - 80{\cdot}00)^2}. \tag{5}$$

It will be noticed that the rotatory power in this formula is expressed as a difference of two very large terms of nearly equal magnitude but of opposite signs involving two absorption wavelengths respectively at 1129 Å and 1099 Å and that the influence of the infrared has been retained. The formula, however, deviates notably from the newer measurements of Servant (*loc. cit.*) in the far ultraviolet region. Servant (1940) has therefore fitted his results with the expression

$$\rho = 10^4 \frac{10^{-6}\lambda^2 + 0{\cdot}515}{(13{\cdot}956 \times 10^{-2}\lambda^4 - 17639 \times 10^{-6}\lambda^2 + 2{\cdot}076)} \tag{6}$$

where λ is the wavelength of light in vacuum expressed in Å. He has assumed the existence of two characteristic wavelengths, one at 1064 Å, and another at 362 Å. The formula fits the entire data from 7000 Å to 1500 Å well. Later, the same author (1941), realising that a multiterm formula involving numerous unknown constants is very artificial and arbitrary, has rejected (6) in favour of the simpler formula

$$\rho = (n_0^2 + 2) \frac{165{\cdot}6}{10^{-6}\lambda^2 - 1{\cdot}325}, \tag{7}$$

where n_0 is the ordinary refractive index of quartz. The characteristic absorption assumed here lies at 1150 Å. The formula is approximately valid from 8000 Å to 2000 Å and fails farther out in the ultraviolet.

Finally, Radhakrishnan (1947) has proposed the formula

$$\rho = \frac{4{\cdot}948}{\lambda^2 - 0{\cdot}014161} + \frac{4{\cdot}617}{\lambda^2 - 0{\cdot}011236} - \frac{2{\cdot}311}{\lambda^2 - 0{\cdot}000974}$$

$$- \frac{0{\cdot}000815}{(\lambda^2 - 0{\cdot}0195)^2} - 0{\cdot}1905. \tag{8}$$

This one is largely a refinement on the work of Lowry and Coode-Adams. The absorption at 312 Å is still retained, but the single term at 1129 Å has been split into two terms at 1060 Å and 1190 Å. In addition a square term at about 1400 Å, almost at the limit of continuous absorption of light in quartz, has been introduced. The formula gives a tolerable fit.

Thus we see that a variety of formulæ involving numerous hypothetical absorption frequencies have been suggested to express the rotatory dispersion of quartz. Even a cursory examination of these formulæ shows that most of them are extremely complicated and arbitrary in character and all, except one, are unsatisfactory in accounting for the actual observed facts. Apart from this, there is an even more serious objection which may be raised against them.

KUHN'S SUMMATION RULE

A fundamental theorem concerning the optical rotatory power of molecular systems was derived by Kuhn (1929) in the first instance by considering the behaviour of a model consisting of two coupled resonators. The theorem states that the sum of the numerators determining the contributions of the different absorption frequencies to the rotatory power should vanish, *i.e.*,

if

$$\rho = \sum_r \frac{a_r \nu^2}{\nu_r^2 - \nu^2}, \tag{9}$$

then

$$\sum_r a_r = 0.$$

Proofs of this summation rule involving no special assumptions regarding the molecular model have since been given by several authors (*vide* reviews by Condon, 1937; Kauzmann, Walter and Eyring, 1940; Mathieu, 1946).

It is clear that the criterion furnished by this summation rule should be taken into account in deriving any formula, theoretical or empirical, which

claims to express rotatory dispersion. Without entering into the detailed numerical calculations, even a rough estimate of

$$\sum_r a_r \left(= \sum_r Q_r/\lambda_r^2\right)$$

in formulæ (1)–(8) shows that the summation rule is far from fulfilled by any one of them. As there is little justification in working out complicated expressions if we do not restrict ourselves to the basic requirement of the theory we may conclude that all the earlier formulæ are wholly inappropriate for the case of quartz.

A New Formula

The present writer has found (1952, 1954 *b*) that the rotatory dispersion of quartz from the visible to the extreme ultraviolet region of the spectrum is accurately represented by a simple formula involving only two constants, *viz.*,

$$\rho = \frac{k\lambda^2}{(\lambda^2 - \lambda_0^2)^2}. \qquad (10)$$

The formula approximates to Biot's Law when $\lambda \gg \lambda_0$. Also for a given value of λ_0, the rate of variation of the rotatory power with wavelength in this formula is much greater than in the Drude type of formula. The constants which the experimental data are

$$k = 7{\cdot}19, \qquad \lambda_0^2 = 0{\cdot}00858 \qquad \text{or} \qquad \lambda_0 = 0{\cdot}0926283\,\mu.$$

Here ρ is in degrees per millimetre and λ is in microns. The correct procedure is to express λ as the wavelength of light in vacuum. Servant has done so for his measurements in the remote ultraviolet, but the other authors have given the wavelengths in air. However, in the process of trying to fit a rotatory dispersion formula, Servant has effected the necessary corrections for a few wavelengths, extending from 1525 Å to 7000 Å. The rotatory powers for these wavelengths along with the values calculated with the above formula are set out below (Table I).

The agreement is very good from 6000 Å to 1525 Å. The error in this range, which never exceeds about two parts in a thousand, *is not of a progressive nature*. Data are available for many more wavelengths. The present writer (1954 *c*) has verified the validity of the formula for over 80 wavelengths extending from 6000 Å to 1520 Å. The fit is found to be extremely good over this range, the error being sometimes positive, sometimes negative. There is a slight discrepancy as we proceed towards the

TABLE I

$\lambda_{vac.}$ (in μ)	ρ (expt.)	ρ (calc.)	ρ (expt.)—ρ (calc.)
·1525	776·0	776·3	−0·3
·1550	724·0	724·1	−0·1
·1650	564·5	563·1	+1·4
·1750	453·5	453·1	+0·4
·1850	374·0	374·2	−0·2
·1950	315·5	315·3	+0·2
·2000	291·3	291·3	±0·0
·2250	205·9	205·9	±0·0
·2500	154·60	154·56	+0·04
·3000	97·72	97·61	+0·11
·4000	50·26	50·17	+0·09
·5000	30·86	30·84	+0·02
·6000	20·93	20·96	−0·03
·7000	15·13	15·20	−0·07

infrared from the red end of the spectrum. This is no doubt due to the contribution of the infrared bands which have not been included in the above formula. Lowry's measurements upto $3{\cdot}7\,\mu$ definitely indicate the necessity of introducing a small infrared term.

It can easily be shown that the single characteristic wavelength at $0{\cdot}0926283\,\mu$ used in the above formula lies in the region of the spectrum in which the ultraviolet bands of quartz appear. A one-term dispersion formula for the ordinary refractive index of quartz has been fitted up using this same wavelength. The formula proposed is of the Sellmeier-Drude type which is theoretically valid irrespective of whether a polarisation field exists or not (Krishnan and Roy, 1956). The formula is

$$n_\omega^2 - 1 = \frac{1{\cdot}35\,\lambda^2}{\lambda^2 - \lambda_0^2}, \tag{11}$$

where

$$\lambda_0^2 = 0{\cdot}00858.$$

λ (in μ)	n_ω (expt.)	n_ω (calc.)
·18547	1·676	1·673
·20006	1·649	1·649
·21107	1·634	1·635
·2428	1·605	1·606
·3034	1·577	1·578
·3587	1·564	1·564
·4800	1·550	1·550
·5893	1·544	1·544
·7065	1·540	1·540
·8447	1·538	1·538

The agreement is reasonably good over the whole range. This indicates that the characteristic wavelength at $0{\cdot}0926283\,\mu$ is approximately the effective average of the absorption spectrum of quartz in the ultraviolet. Of course, it is well known that the average characteristic wavelength operative in refractive dispersion and in rotatory dispersion formulæ need not necessarily be the same, simply because the form of the expressions in the two cases are different (Condon, *loc. cit.*), but in the particular case of quartz they happen to roughly coincide.

The rotatory power normal to the optic axis was measured for the first time by Voigt (1905). There have been a number of subsequent measurements, the most recent being those of Bruhat and Weil (1936), who have summarised their results as follows: the ratio of the rotatory powers of quartz perpendicular and parallel to the optic axis is independent of the wavelength for the spectral interval 5780 Å – 2 40 Å, the ratio being—0·54 to within an accuracy of 0·5%.

Evidently, the rotatory dispersion normal to the optic axis should also be expressible by a formula of the same type as (10) with λ_0 unaltered and k reduced in the ratio of—0·54.

DISCUSSION

In their article in the *Handbuch der Physik*, Born and Goppert-Mayer (1933) arrive at the general formula

$$\rho = \sum_r \frac{P_r \lambda^2}{(\lambda^2 - \lambda_r^2)^2} + \frac{Q_r}{(\lambda^2 - \lambda_r^2)} + \sum_v \frac{P_v \lambda^2}{(\lambda^2 - \lambda_v^2)^2} + \frac{Q_v}{(\lambda^2 - \lambda_v^2)} \quad (12)$$

It will be noticed that in addition to terms of the Drude type certain quadratic terms of the same form as suggested earlier are also present. We have now discovered that these terms play a predominant role in determining the rotatory dispersion of quartz. The simplicity of the new formula and the accuracy of its fit clearly shows that terms of the Drude type do not contribute in any observable measure to the rotatory power of quartz in the visible and ultraviolet region of the spectrum.

After this work had been completed, it was found on going through some of the very early literature on the subject that in 1883 Lommel had suggested a formula of the type

$$\rho = \frac{a\lambda^2}{(\lambda^2 - \lambda_0^2)^2}$$

for quartz and a few optically active liquids. He found that the available data for quartz from 8000 Å to 2200 Å were expressed tolerably well when $\log a = 0{\cdot}8555912$ or $a = 7{\cdot}17119$ and $\log \lambda_0^2 = 7{\cdot}9341257 - 10$ or $\lambda_0 = 0{\cdot}0928032\,\mu$.

Lommel's work has apparently been overlooked by most of the authors who have since been interested in this crystal. We have now found that this formula fits the data even up to the extreme ultraviolet. In addition, as we shall see later, we have been able to give it a theoretical basis while actually Lommel's work was done before any proper theory of optical activity had yet been put forward.

THE THEORY OF COUPLED OSCILLATORS

The idea that optical activity arises from a particular spatial distribution of coupled oscillators was developed by Born, Oseen, Gray, de Mallemann and others (*vide* reviews by Condon, *loc. cit.*; Kauzmann, *et al.*, *loc. cit.*; Mathieu, *loc. cit.*). Later, Kuhn contributed greatly to the subject by putting forward a simple model which demonstrated all the essential features of the phenomenon. Kuhn's model consists of two linear anisotropic resonators having natural frequencies of free vibration ν_1 and ν_2 respectively which are coupled with each other. Each resonator

is a charged particle which is assumed to be bound elastically to its own equilibrium position and capable of vibrating along a line. The analysis shows that the system has two modes of vibration, in each of which both resonators take part, one with frequency ν_1 and the other with frequency ν_2. The contributions of the two modes to the rotatory power turn out to be of opposite signs when the frequency of the incident light is less than that of either resonator.

In this model ν_1 and ν_2 are assumed to be very different, so that the change of frequency brought about by the mutual coupling has been neglected altogether. This is, however, not permissible when ν_1 and ν_2 are very close to each other. In fact, in the limiting case when $\nu_1 = \nu_2$, each frequency is actually split into a doublet, the magnitude of the splitting being dependent on the strength of the interaction between the resonators.

We shall now discuss the optical behaviour of two identical linear anisotropic resonators coupled with each other. Let the natural frequency of vibration of the charged particle in each resonator be ν_0, when uncoupled. As a result of the coupling, ν_0 would be split into two frequencies ν_1 and ν_2. In one normal mode of vibration, the particles in the two resonators would vibrate with equal amplitude and in the same phase, and in the other normal mode they would vibrate with equal amplitude but opposite in phase.

Let the first resonator be situated at the origin of the co-ordinate system and let its vibration direction be OX. Let the second resonator be at $(0, 0, d)$ with its vibration direction parallel to OY. Suppose the charge and mass of the particle in each resonator to be q and M respectively. For convenience, we shall put $q = fe$ and $\mathrm{M} = fm$, where e and m are the charge and mass of the electron and f the oscillator strength. We shall call this coupled system the *compound* resonator. Let us examine the action of a light wave on such a compound resonator.

Let right circular light given by

$$x = \mathrm{E}_0 \cos \omega t$$

$$y = -\mathrm{E}_0 \sin \omega t$$

be incident along OZ. The force exerted by the light wave on the charged particle of the first resonator is

$$\mathrm{F}_1 = fe\,\mathrm{E}_0 \cos \omega t.$$

The force on the charged particle of the second resonator which is rotated through 90° about the Z axis with respect to the first one is

$$\mathrm{F}_2 = -fe\,\mathrm{E}_0 \sin (\omega t - \phi),$$

where

$$\phi = \frac{2\pi\bar{n}d}{\lambda},$$

$\bar{n}$ being the mean refractive index of the medium. Since ϕ is small

$$F_2 = -fe\,E_0(\sin\omega t - \phi\cos\omega t).$$

Now, the compound resonator has two normal modes of vibration and the force may be expressed in terms of the two normal co-ordinates as

$$R_{\xi_1} = \frac{1}{\sqrt{2}}(F_1 + F_2)$$

$$R_{\xi_2} = \frac{1}{\sqrt{2}}(F_1 - F_2)$$

Substituting for F_1 and F_2, we get

$$R_{\xi_1} = \frac{fe\,E_0}{\sqrt{2}}[(1+\phi)\cos\omega t - \sin\omega t]$$

$$= a^r{}_{\xi_1}\, fe\,E_0\cos(\omega t + \sigma),$$

where $(a^r{}_{\xi_1})^2 = (1+\phi)$, neglecting higher powers of ϕ. Hence, the equation of motion of the particles would be of the form

$$\ddot{\xi}_1 + \omega_1{}^2\xi_1 = a^r{}_{\xi_1}\frac{fe\,E_0}{M}\cos(\omega t + \sigma).$$

Therefore,

$$\xi_1 = \frac{a^r{}_{\xi_1}\, fe\,E_0\cos(\omega t + \sigma)}{M(\omega_1{}^2 - \omega^2)}$$

Hence, the dipole moment induced

$$= (a^r{}_{\xi_1}\, fe)^2\frac{E_0}{M(\omega_1{}^2 - \omega^2)}$$

$$= (a^r{}_{\xi_1})^2\, f\frac{e^2}{m}\frac{E_0}{\omega_1{}^2 - \omega^2}$$

putting $M = fm$. The dipole moment could be expressed as two components at right angles to each other, say m_g and m_k, where

$$m_g = f\frac{e^2}{m}\frac{E_0}{\omega_1{}^2 - \omega^2}.$$

and

$$m_k = \phi f \frac{e^2}{m} \frac{E_0}{\omega_1^2 - \omega^2}.$$

These results are for a single compound resonator. If there are N such compound resonators all lying with their axes parallel to OZ but assuming different orientations about it, the mean polarisability per unit volume would be $N(m_g + m_k)/2E_0$.

Hence

$$(n_r^2 - 1)_{\xi_1} = 2\pi N (a^r_{\xi_1})^2 \frac{e^2}{m} \frac{f}{\omega_1^2 - \omega^2}.$$

In a similar manner, we get for the other normal mode

$$(n_r^2 - 1)_{\xi_2} = 2\pi N (a^r_{\xi_2}) \frac{e^2}{m} \frac{f}{\omega_2^2 - \omega^2},$$

where

$$(a^r_{\xi_2})^2 = 1 - \phi.$$

Let us write

$$n_r^2 - 1 = (n_r^2 - 1)_{\xi_1} + (n_r^2 - 1)_{\xi_2}.$$

For left circular light given by

$$x = E_0 \cos \omega t$$
$$y = E_0 \sin \omega t,$$

we have similarly

$$(n_l^2 - 1)_{\xi_1} = 2\pi N (a^l_{\xi_1})^2 \frac{e^2}{m} \frac{f}{\omega_1^2 - \omega^2},$$

$$(n_l^2 - 1)_{\xi_2} = 2\pi N (a^l_{\xi_2})^2 \frac{e^2}{m} \frac{f}{\omega_2^2 - \omega^2},$$

where

$$(a^l_{\xi_1})^2 = 1 - \phi,$$
$$(a^l_{\xi_2})^2 = 1 + \phi,$$

and

$$n_l^2 - 1 = (n_l^2 - 1)_{\xi_1} + (n_l^2 - 1)_{\xi_2}.$$

Therefore,

$$n_l^2 - n_r^2 = 4\pi N \frac{e^2}{m} f \phi \left[\frac{1}{\omega_2^2 - \omega^2} - \frac{1}{\omega_1^2 - \omega^2} \right].$$

It will be noticed that the numerators in the two terms are equal in magnitude but opposite in sign and this is in conformity with Kuhn's summation rule.

Let

$$\omega_1^2 = \omega_0^2 + 2\pi^2\epsilon$$
$$\omega_2^2 = \omega_0^2 - 2\pi^2\epsilon$$

We shall assume that the resonators are not very strongly coupled so that ϵ is a small quantity. Putting

$$n_l + n_r = 2\bar{n}, \quad \phi = \frac{2\pi\bar{n}d}{\lambda}$$

and

$$\omega_0 = 2\pi\,\nu_0,$$

we get

$$n_l - n_r = \frac{Ne^2d}{m\lambda}\frac{f\epsilon}{(\nu_0^2 - \nu^2)^2}$$

neglecting ϵ^2 in the denominator. Hence

$$\rho = \frac{\pi}{\lambda}(n_l - n_r) = \frac{A_0\lambda^2}{(\lambda^2 - \lambda_0^2)^2},$$

where

$$A_0 = \frac{\pi Ne^2d\lambda_0^4 f\epsilon}{mc^4}.$$

If the compound resonators were randomly oriented we would have to introduce a factor $\frac{1}{3}$ in the expression for the rotatory power.

If, as a more general case, we assume that the first resonator (0, 0, 0) has direction cosines α, β, γ and that the second resonator (0, 0, d) is rotated through an angle θ about the Z axis with respect to the first one, it may be shown that

$$\rho = \frac{A_0\lambda^2}{(\lambda^2 - \lambda_0^2)^2}, \tag{13}$$

where

$$A_0 = \frac{\pi Ne^2d\sin\theta\,(\alpha^2 + \beta^2)\,\lambda_0^4 f\epsilon}{3\,mc^4}$$

It will be seen from (13) that the two enantiomorphous forms will have opposite rotatory powers, since $\rho \propto \sin\theta$.

Thus, by means of an extremely elementary model we have been able to derive the correct expression for the rotatory dispersion of quartz. It should be exphasised that the new single term formula intrinsically satisfies Kuhn's summation rule and is therefore more justified than any of the earlier formulæ worked out for this crystal.

We shall now try and interpret these results in terms of the structure of quartz. α-Quartz belongs to the space group D_3^4 or the enantiomorphous D_3^6. The unit cell has three SiO_2 units spaced at equal intervals along the vertical screw axis, each of which is turned through 120° with respect to its predecessor. It is this screw structure which is responsible for its optical activity, the individual constituent units themselves being optically inactive. In view of the foregoing theoretical considerations, it can scarcely be doubted that the rotatory power of quartz arises primarily as a result of an interaction in the nature of a resonance between the similar polarisable units constituting the crystal. This type of interaction causes a splitting of the characteristic frequency of each individual unit and consequently, the rotatory dispersion formula is of the form (13). By a simple extension of the model which we have just considered, it may be shown in an approximate way (Chandrasekhar, 1954 *c*) that for an hypothetical crystal with a screw structure built up of such compound resonators, the rotatory dispersion formula for propagation of light along and normal to the optic axis are both of the quadratic form (13), a result which agrees with the experiments of Bruhat and Weil (*loc. cit.*).

The same type of formula is also found to fit the data for cinnabar, benzil and sodium chlorate (Chandrasekhar, 1953, 1954 *a*, 1954 *c*) quite well and, in fact, much better than any of the previous formulæ proposed for these crystals. It may be remarked that, like quartz, the rotatory power of these crystals is present only in the crystalline state and not in solution.

In conclusion, I have great pleasure in expressing my thanks to Professor Sir C. V. Raman, F.R.S., for the valuable discussions I had with him during the course of these investigations. I am also grateful to Dr. S. Ramaseshan for his kind advice and interest.

References

Born, M. and Goppert-Mayer, M. *Hand. der. Phys.*, 1933, **24** (2), 668.

Bradshaw, T. and Livens, G. H. *Proc. Roy. Soc.*, 1929, **122 A**, 245.

Bruhat, G. and Weil, L. .. *Journ. de Phys. et le Rad.*, 1936, **7**, 12.

Chandrasekhar, S. .. *Proc. Ind. Acad. Sci.*, 1952, **35 A**, 103.

———— .. *Ibid.*, 1953, **37**, 697.

———— .. *Ibid.*, 1954*a*, **39**, 243.

Chandrasekhar, S.	..	*Proc. Ind. Acad. Sci.*, 1954*b*, **39**, 290.
————	..	*D.Sc. Thesis*, Nagpur University, Nagpur, India.
Condon, E. U.	..	*Rev. Mod. Phys.*, 1937, **9**, 432.
Drude, P.	..	"*Lehrbuch der Optik*" (*Leipzig*), 1900.
Duclaux, J. and Jeantet, P.	..	*Journ. de Phys.*, 1926, **7**, 200.
Kauzmann, W. J., Walter, J. E. and Eyring, H.		*Chem. Revs.*, 1940, **26**, 339.
Krishnan, K. S. and Roy, S. K.		*Phil. Mag.*, 1956, **1**, 926.
Kuhn, W.	..	*Z. fur Phys. Chem.*, 1929, **4 B**, 14.
Lommel, E.	..	*Ann. Phys. und Chem.*, 1883, **20**, 578.
Lowry, T. M.	..	*Phil. Trans.* **212 A**, 261.
——— and Coode-Adams, W. R. C.		*Ibid.*, 1927, **226**, 391.
Lowry, T. M.	..	*Optical Rotatory Power*, 1935 (Longmans, Green & Co., London).
Mathieu, J. P.	..	*Les Theories Moleculaires du Pouvoir Rotatoire Naturel*, 1946 (C.N.R.S., Paris).
Radhakrishnan, T.	..	*Proc. Ind. Acad. Sci.*, 1947, **25 A**, 260.
Servant, R.	..	*Ann. de Phys.*, 1939, **12**, 397.
————	..	*Comp. Rend.*, 1940, **211**, 554.
————	..	*Ibid.*, 1941, **212**, 1140.
Sosman, R. B.	..	*The Properties of Silica*, 1927, (A.C.S. Monographs).
Voigt, W.	..	*Ann. der Phys.*, 1905, **18**, 645.

PROBLEMS ON THE MOTION OF NON-NEWTONIAN VISCOUS LIQUIDS

General Considerations

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0. Introduction

The classical study of the hydrodynamical behaviour of viscous liquids is based on the Navier Stokes Equations of motion,

$$\rho\left(\frac{\delta}{\delta t}+u\frac{\delta}{\delta x}+v\frac{\delta}{\delta y}+w\frac{\delta}{\delta z}\right)(u,\ v,\ w)=\rho\,(\mathrm{X},\ \mathrm{Y},\ \mathrm{Z}) - \text{grad}\ p+\mu\Delta\,(u,\ v,\ w) \tag{0.1}$$

and the continuity equation

$$\text{div}\,(u,\ v,\ w)=0. \tag{0.2}$$

The equations (0.1) follow by the application of Newton's second law of motion to an element of the liquid and the use of the relation

$$t_j^{\,i}=+\,\mathrm{F}_0\delta_j^{\,i}+\mathrm{F}_1 d_j^{\,i} \tag{0.3}$$

between the stress tensor $t_j^{\,i}$ and the tensor of rate of deformation

$$d_j^{\,i}=\tfrac{1}{2}\left(\frac{\delta u^i}{\delta x^j}+\frac{\delta u^j}{\delta x^i}\right), \tag{0.4}$$

where $\delta_j^{\,i}$ are Kronecker deltas,

$$\delta_j^{\,i}=0,\ \ (i\neq j);=1,\ \ (i=j),$$

u^1, u^2, u^3; x^1, x^2, x^3 stand for u, v, w; x, y, z

respectively, and F_0, F_1 are functions of some material constants, as well as the invariants of the tensor $d_j^{\,i}$. Experimental evidence of the behaviour of some *very viscous liquids* noticed during the last decade led Reiner and others to examine the hydrodynamics of such general or non-Newtonian vicsous liquids. Reiner[1] has established thoroughly, that the most general relation between the stress tensor $t_j^{\,i}$ and the tensor of the rate of deformation $d_j^{\,i}$ has the form

$$t_j^{\,i}=+\,\mathrm{F}_0\delta_j^{\,i}+\mathrm{F}_1 d_j^{\,i}+\mathrm{F}_2 d_a^{\,i}d_j^{\,a}, \tag{0.5}$$

which is a generalization of (0.4), including the additional term $F_2 d_a{}^i d_j{}^a$. The presence of the coefficient F_2 gives rise to the phenomenon of 'cross-viscosity'. Writing $F_0 = -p$, $F_1 = 2\mu$, $F_2 = 2\mu_c$ we recognize p, μ and μ_c to be the mean pressure, the coefficient of viscosity and the coefficient of cross viscosity.

1. THE EQUATIONS OF MOTION

Adopting the relation (0.5) instead of (0.3) and replacing F_0, F_1, F_2 in the above specified way, we write the equations of motion of non-Newtonian viscous liquids in the form

$$\rho\left(\frac{\delta}{\delta t} + u\frac{\delta}{\delta x} + v\frac{\delta}{\delta y} + w\frac{\delta}{\delta z}\right)(u,\ v,\ w)$$

$$= \rho\,(X,\ Y,\ Z) - \text{grad}\ p + \mu\Delta\,(u,\ v,\ w) + 2\mu_c\ \text{div}\ (d_a{}^i d_j{}^a).$$

The vector div $(d_a{}^i d_j{}^a)$ has the components

$$\frac{\delta}{\delta x}[(d_1{}^1)^2 + (d_2{}^1)^2 + (d_3{}^1)^2] + \frac{\delta}{\delta y}[d_1{}^1 d_2{}^1 + d_2{}^1 d_2{}^2 + d_3{}^1 d_3{}^2]$$

$$+ \frac{\delta}{\delta z}[d_1{}^1 d_3{}^1 + d_2{}^1 d_3{}^2 + d_3{}^1 d_3{}^3],$$

$$\frac{\delta}{\delta x}[d_1{}^1 d_2{}^1 + d_2{}^1 d_2{}^2 + d_3{}^1 d_3{}^2] + \frac{\delta}{\delta y}[(d_2{}^1)^2 + (d_2{}^2)^2 + (d_3{}^2)^2]$$

$$+ \frac{\delta}{\delta z}[d_2{}^1 d_3{}^1 + d_2{}^2 d_3{}^2 + d_3{}^2 d_3{}^3],$$

$$\frac{\delta}{\delta x}[d_1{}^1 d_3{}^1 + d_2{}^1 d_3{}^2 + d_3{}^1 d_3{}^3] + \frac{\delta}{\delta y}[d_2{}^1 d_3{}^1 + d_2{}^2 d_3{}^2 + d_3{}^2 d_3{}^3]$$

$$+ \frac{\delta}{\delta z}[(d_3{}^1)^2 + (d_3{}^2)^2 + (d_3{}^3)^2].$$

Substituting for $d_j{}^i$ from (0.4) and using the continuity equation, *viz.*,

$$d_1{}^1 + d_2{}^2 + d_3{}^3 = 0,$$

we obtain after simplification the following equations of motion in the Cartesian form:

$$\rho\left(\frac{\delta u}{\delta t}+u\frac{\delta u}{\delta x}+v\frac{\delta u}{\delta y}+w\frac{\delta u}{\delta z}\right)$$

$$=\rho X-\frac{\delta p}{\delta x}+\mu\Delta u+\tfrac{1}{2}\mu_c\left\{\frac{\delta}{\delta x}\left[4\left(\frac{\delta u}{\delta x}\right)^2+\left(\frac{\delta u}{\delta z}+\frac{\delta w}{\delta x}\right)^2\right.\right.$$

$$\left.+\left(\frac{\delta v}{\delta x}+\frac{\delta u}{\delta y}\right)^2\right]-2\frac{\delta v}{\delta y}\frac{\delta}{\delta z}\left(\frac{\delta u}{\delta z}+\frac{\delta w}{\delta x}\right)$$

$$-2\frac{\delta w}{\delta z}\frac{\delta}{\delta y}\left(\frac{\delta v}{\delta x}+\frac{\delta u}{\delta y}\right)+\left(\frac{\delta w}{\delta y}+\frac{\delta v}{\delta z}\right)\left[\frac{\delta}{\delta y}\left(\frac{\delta u}{\delta z}+\frac{\delta w}{\delta x}\right)\right.$$

$$\left.+\frac{\delta}{\delta z}\left(\frac{\delta v}{\delta x}+\frac{\delta u}{\delta y}\right)\right]+\left(\frac{\delta u}{\delta z}+\frac{\delta w}{\delta x}\right)\frac{\delta\xi}{\delta y}$$

$$\left.-\left(\frac{\delta v}{\delta x}+\frac{\delta u}{\delta y}\right)\frac{\delta\xi}{\delta z}\right\}, \tag{1.1}$$

$$\rho\left(\frac{\delta v}{\delta t}+u\frac{\delta v}{\delta x}+v\frac{\delta v}{\delta y}+w\frac{\delta v}{\delta z}\right)$$

$$=\rho Y-\frac{\delta p}{\delta y}+\mu\Delta v+\tfrac{1}{2}\mu_c\left\{\frac{\delta}{\delta y}\left[4\left(\frac{\delta v}{\delta y}\right)^2+\left(\frac{\delta v}{\delta x}+\frac{\delta u}{\delta y}\right)^2\right.\right.$$

$$\left.+\left(\frac{\delta w}{\delta y}+\frac{\delta v}{\delta z}\right)^2\right]-2\frac{\delta w}{\delta z}\frac{\delta}{\delta x}\left(\frac{\delta v}{\delta x}+\frac{\delta u}{\delta y}\right)$$

$$-2\frac{\delta u}{\delta x}\frac{\delta}{\delta z}\left(\frac{\delta w}{\delta y}+\frac{\delta v}{\delta z}\right)+\left(\frac{\delta u}{\delta z}+\frac{\delta w}{\delta x}\right)\left[\frac{\delta}{\delta z}\left(\frac{\delta v}{\delta x}+\frac{\delta u}{\delta y}\right)\right.$$

$$\left.+\frac{\delta}{\delta x}\left(\frac{\delta w}{\delta y}+\frac{\partial v}{\partial z}\right)\right]+\left(\frac{\delta v}{\delta x}+\frac{\delta u}{\delta y}\right)\frac{\delta\eta}{\delta z}$$

$$\left.-\left(\frac{\delta w}{\delta y}+\frac{\delta v}{\delta z}\right)\frac{\delta\eta}{\delta x}\right\}, \tag{1.2}$$

$$\rho\left(\frac{\delta w}{\delta t}+u\frac{\delta w}{\delta x}+v\frac{\delta w}{\delta y}+w\frac{\delta w}{\delta z}\right)$$

$$=\rho Z-\frac{\delta p}{\delta z}+\mu\,\Delta w+\tfrac{1}{2}\mu_c\left\{\frac{\delta}{\delta z}\left[4\left(\frac{\delta w}{\delta z}\right)^2+\left(\frac{\delta w}{\delta y}+\frac{\delta v}{\delta z}\right)^2\right.\right.$$

$$\left.+\left(\frac{\delta u}{\delta z}+\frac{\delta w}{\delta x}\right)^2\right]-2\frac{\delta u}{\delta x}\frac{\delta}{\delta y}\left(\frac{\delta w}{\delta y}+\frac{\delta v}{\delta z}\right)$$

$$- 2\frac{\delta v}{\delta y}\frac{\delta}{\delta x}\left(\frac{\delta u}{\delta z}+\frac{\delta w}{\delta x}\right)+\left(\frac{\delta v}{\delta x}+\frac{\delta u}{\delta y}\right)\left[\frac{\delta}{\delta x}\left(\frac{\delta w}{\delta y}+\frac{\delta v}{\delta z}\right)\right.$$

$$\left.+\frac{\delta}{\delta y}\left(\frac{\delta u}{\delta z}+\frac{\delta w}{\delta x}\right)\right]+\left(\frac{\delta w}{\delta y}+\frac{\delta v}{\delta z}\right)\frac{\delta\zeta}{\delta x}$$

$$-\left(\frac{\delta u}{\delta z}+\frac{\delta w}{\delta x}\right)\frac{\delta\zeta}{\delta y}\Big\}. \tag{1.3}$$

When the external forces belong to a conservative field and are derivable from a force potential Ω, we may write the equations also in the form

$$\frac{\delta u}{\delta t}-v\zeta+w\eta$$

$$=-\frac{\delta}{\delta x}\left(\Omega+\frac{p}{\rho}+\tfrac{1}{2}q^2\right)+\nu\Delta u+\tfrac{1}{2}\nu_c\left\{\frac{\delta}{\delta x}\left[4\left(\frac{\delta u}{\delta x}\right)^2\right.\right.$$

$$\left.+\left(\frac{\delta u}{\delta z}+\frac{\delta w}{\delta x}\right)^2+\left(\frac{\delta v}{\delta x}+\frac{\delta u}{\delta y}\right)^2\right]-2\frac{\delta v}{\delta y}\frac{\delta}{\delta z}\left(\frac{\delta u}{\delta z}+\frac{\delta w}{\delta z}\right)$$

$$-2\frac{\delta w}{\delta z}\frac{\delta}{\delta y}\left(\frac{\delta v}{\delta x}+\frac{\delta u}{\delta y}\right)+\left(\frac{\delta w}{\delta y}+\frac{\delta v}{\delta z}\right)\left[\frac{\delta}{\delta y}\left(\frac{\delta u}{\delta z}+\frac{\delta w}{\delta x}\right)\right.$$

$$\left.+\frac{\delta}{\delta z}\left(\frac{\delta v}{\delta x}+\frac{\delta u}{\delta y}\right)\right]+\left(\frac{\delta u}{\delta z}+\frac{\delta w}{\delta x}\right)\frac{\delta\xi}{\delta y}$$

$$\left.-\left(\frac{\delta v}{\delta x}+\frac{\delta u}{\delta y}\right)\frac{\delta\xi}{\delta z}\right\}, \tag{1.4}$$

$$\frac{\delta v}{\delta t}-w\xi+u\zeta$$

$$=-\frac{\delta}{\delta y}\left(\Omega+\frac{p}{\rho}+\tfrac{1}{2}q^2\right)+\nu\Delta v+\tfrac{1}{2}\nu_c\left\{\frac{\delta}{\delta y}\left[4\left(\frac{\delta v}{\delta y}\right)^2\right.\right.$$

$$\left.+\left(\frac{\partial v}{\partial x}+\frac{\delta u}{\delta y}\right)^2+\left(\frac{\delta w}{\delta y}+\frac{\delta v}{\delta z}\right)^2\right]-2\frac{\delta w}{\delta z}\frac{\delta}{\delta x}\left(\frac{\delta v}{\delta x}+\frac{\delta u}{\delta y}\right)$$

$$-2\frac{\delta u}{\delta x}\frac{\delta}{\delta z}\left(\frac{\delta w}{\delta y}+\frac{\delta v}{\delta z}\right)+\left(\frac{\delta u}{\delta z}+\frac{\delta w}{\delta x}\right)\left[\frac{\delta}{\delta z}\left(\frac{\delta v}{\delta x}+\frac{\delta u}{\delta y}\right)\right.$$

$$\left.+\frac{\delta}{\delta y}\left(\frac{\delta w}{\delta y}+\frac{\delta v}{\delta z}\right)\right]+\left(\frac{\delta v}{\delta x}+\frac{\delta u}{\delta y}\right)\frac{\delta\eta}{\delta z}$$

$$\left.-\left(\frac{\delta w}{\delta y}+\frac{\delta v}{\delta z}\right)\frac{\delta\eta}{\delta x}\right\}, \tag{1.5}$$

$$\frac{\delta w}{\delta t} - u\eta + v\xi$$

$$= -\frac{\delta}{\delta z}\left(\Omega + \frac{p}{\rho} + \tfrac{1}{2}q^2\right) + \nu\Delta w + \tfrac{1}{2}\nu_c\left\{\frac{\delta}{\delta z}\left[4\left(\frac{\delta w}{\delta z}\right)^2\right.\right.$$

$$\left. + \left(\frac{\delta w}{\delta y} + \frac{\delta v}{\delta z}\right)^2 + \left(\frac{\delta u}{\delta z} + \frac{\delta w}{\delta x}\right)^2\right] - 2\frac{\delta u}{\delta x}\frac{\delta}{\delta y}\left(\frac{\delta w}{\delta y} + \frac{\delta v}{\delta z}\right)$$

$$- 2\frac{\delta v}{\delta y}\frac{\delta}{\delta x}\left(\frac{\delta u}{\delta z} + \frac{\delta w}{\delta x}\right) + \left(\frac{\delta v}{\delta x} + \frac{\delta u}{\delta y}\right)\left[\frac{\delta}{\delta x}\left(\frac{\delta w}{\delta y} + \frac{\delta v}{\delta z}\right)\right.$$

$$\left. + \frac{\delta}{\delta y}\left(\frac{\delta u}{\delta z} + \frac{\delta w}{\delta x}\right)\right] + \left(\frac{\delta w}{\delta y} + \frac{\delta v}{\delta z}\right)\frac{\delta \zeta}{\delta x}$$

$$\left. - \left(\frac{\delta u}{\delta z} + \frac{\delta w}{\delta x}\right)\frac{\delta \zeta}{\delta y}\right\}. \tag{1.6}$$

2. Plane Motion

The above equations get remarkably simplified in the case of plane motion. If the motion is in planes parallel to the xoy plane we have $w = 0$ and all the quantities are independent of z. The equations of motion then assume the form

$$\frac{\delta u}{\delta t} - v\zeta = -\frac{\delta}{\delta x}\left(\Omega + \frac{p}{\rho} + \tfrac{1}{2}q^2\right) + \nu\Delta u + \tfrac{1}{2}\nu_c\left\{\frac{\delta}{\delta x}\left[4\left(\frac{\delta u}{\delta x}\right)^2\right.\right.$$

$$\left.\left. + \left(\frac{\delta v}{\delta x} + \frac{\delta u}{\delta y}\right)^2\right]\right\}, \tag{2.1}$$

$$\frac{\delta v}{\delta t} + u\zeta = -\frac{\delta}{\delta y}\left(\Omega + \frac{p}{\rho} + \tfrac{1}{2}q^2\right) + \nu\Delta v + \tfrac{1}{2}\nu_c\left\{\frac{\delta}{\delta y}\left[4\left(\frac{\delta v}{\delta y}\right)^2\right.\right.$$

$$\left.\left. + \left(\frac{\delta v}{\delta x} + \frac{\delta u}{\delta y}\right)^2\right]\right\}. \tag{2.2}$$

As

$$\frac{\delta u}{\delta x} + \frac{\delta v}{\delta y} = 0,$$

these equations can also be put in the form

$$\frac{\delta}{\delta t}(u,\ v) - (u,\ v,\ 0) \times (0,\ 0,\ \zeta)$$

$$= -\left(\frac{\delta}{\delta x},\ \frac{\delta}{\delta y}\right)\left(\Omega + \frac{p}{\rho} + \tfrac{1}{2}q^2\right) + \tfrac{1}{2}\nu_c\left(\frac{\delta}{\delta x},\ \frac{\delta}{\delta y}\right)$$

$$\cdot\left[-4\left(\frac{\delta u}{\delta x}\right)\left(\frac{\delta v}{\delta y}\right) + \left(\frac{\delta v}{\delta x} + \frac{\delta u}{\delta y}\right)^2\right] + \nu\Delta(u,\ v). \tag{2.3}$$

From this we see by cross-differentiation, that the equation for vorticity in plane motions is given by

$$\frac{\delta\zeta}{\delta t} + u\frac{\delta\zeta}{\delta x} + v\frac{\delta\zeta}{\delta y} = \nu\Delta\zeta, \tag{2.4}$$

which is identical with the corresponding equation in the plane motions of classical or ordinary viscous liquids. It is significant that the cross-viscosity coefficient does not appear in this equation.

If $C = \int \vec{q} \cdot d\vec{r}$ denotes the circulation of the fluid around any closed circuit, we may calculate $d/dt\, C$ in the usual way. While this expression has an awkwardly long form in three dimensions, it assumes a simple, neat form in the case of plane flows. We have in fact,

$$\frac{d}{dt}(\text{circulation}) = \nu \int (\Delta u dx + \Delta v dy) \tag{2.5}$$

so that the circulation is conserved in plane motions if, and only if, $\Delta u dx + \Delta v dy$ is a perfect differential, or equivalently if the vorticity is a harmonic function.

We may also examine here the conditions under which two non-Newtonian viscous plane motions are additive.* If $(u_1, v_1, \zeta_1, p_1, \Omega_1)$ and $(u_2, v_2, \zeta_2, p_2, \Omega_2)$ are the velocity components, vorticities, mean pressures and external force potentials respectively for two plane motions which are additive and π is the adjusted pressure, we have from (2.1), (2.2)

$$\begin{aligned} &\nu_1\zeta_2 + \nu_2\zeta_1 \\ &\quad = \frac{\delta}{\delta x}\left(\frac{\pi}{\rho} + u_1u_2 + v_1v_2\right) + \tfrac{1}{2}\nu_c\left\{ - \frac{\delta}{\delta x}\left[8\frac{\delta u_1}{\delta x}\frac{\delta u_2}{\delta x}\right.\right. \\ &\qquad \left.\left. + 2\left(\frac{\delta v_1}{\delta x} + \frac{\delta u_1}{\delta y}\right)\left(\frac{\delta v_2}{\delta x} + \frac{\delta u_2}{\delta y}\right)\right]\right\}, \\ &-(u_1\zeta_2 + u_2\zeta_1) \\ &\quad = \frac{\delta}{\delta y}\left(\frac{\pi}{\rho} + u_1u_2 + v_1v_2\right) + \tfrac{1}{2}\nu_c\left\{ - \frac{\delta}{\delta y}\left[8\frac{\delta v_1}{\delta y}\frac{\delta v_2}{\delta y}\right.\right. \\ &\qquad \left.\left. + 2\left(\frac{\delta v_1}{\delta x} + \frac{\delta u_1}{\delta y}\right)\left(\frac{\delta v_2}{\delta x} + \frac{\delta u_2}{\delta y}\right)\right]\right\}. \end{aligned}$$

* After completion of the work in this paper we have noticed that A. C. Srivastava has also examined the question of "Superposability in Non-Newtonian Fluids," *vide Abstracts of the Second Congress on Theoretical and Applied Mechanics*, New Delhi (October 1956). The details of his work are, however, not known to us.

Hence we obtain the following equation for determining the adjusted pressure π.

$$d\left(\frac{\pi}{\rho}\right) = (v_1\zeta_2 + v_2\zeta_1)\,dx - (u_1\zeta_2 + u_2\zeta_1)\,dy - d(u_1u_2 + v_1v_2)$$

$$+ \nu_c d\left[2\left(\frac{\delta u_1}{\delta x}\frac{\delta u_2}{\delta x} + \frac{\delta v_1}{\delta y}\frac{\delta v_2}{\delta y}\right) + \left(\frac{\delta v_1}{\delta x} + \frac{\partial u_1}{\partial y}\right)\left(\frac{\partial v_2}{\partial x} + \frac{\partial u_2}{\partial y}\right)\right].$$

In order that this differential equation may lead to the determination of a single-valued function π, $(v_1\zeta_2 + v_2\zeta_1)\,dx - (u_1\zeta_2 + u_2\zeta_1)\,dy$ must be an exact differential. Hence the condition for additivity of two plane motions is given by

$$\frac{\delta}{\delta x}(u_1\zeta_2 + u_2\zeta_1) + \frac{\delta}{\delta y}(v_1\zeta_2 + v_2\zeta_1) = 0,$$

which is the same as in the case of the ordinary viscous liquids.

3. We note here that the expressions arising in the equations of motion due to the cross-viscosity cannot be simplified any further than what we have recorded in (1.4), (1.5), (1.6) and as such the discussion of the general spatial flow with reference to vorticity, additivity of motion and circulation involves cumbersome, though straightforward analysis. However, on actually writing the equations determining the vorticity components we find that, unlike the plane motion, the cross-viscosity does make non-zero contributions to them. We are not reporting these equations on account of their bulk.

4. Dissipation of Energy

If $\delta x\ \delta y\ \delta z$ denotes a rectangular parallelopipedal element of fluid at time t, with centre at (x, y, z) and t_j^i is the stress tensor, then the rate of work on the faces of the element by the tractions is given by

$$\left[\frac{\delta}{\delta x}(t_1^1 u + t_2^1 v + t_3^1 w) + \frac{\delta}{\delta y}(t_1^2 u + t_2^2 v + t_3^2 w)\right.$$

$$\left. + \frac{\delta}{\delta z}(t_1^3 u + t_2^3 v + t_3^3 w)\right]\delta x\,\delta y\,\delta z$$

$$= \left\{\left(\frac{\delta t_1^1}{\delta x} + \frac{\delta t_1^2}{\delta y} + \frac{\delta t_1^3}{\delta z}\right)u + \left(\frac{\delta t_2^1}{\delta x} + \frac{\delta t_2^2}{\delta y} + \frac{\delta t_2^3}{\delta z}\right)v\right.$$

$$\left. + \left(\frac{\delta t_3^1}{\delta x} + \frac{\delta t_3^2}{\delta y} + \frac{\delta t_3^3}{\delta z}\right)w\right\}\delta x\,\delta y\,\delta z$$

$$+\left(t_1{}^1\frac{\delta u}{\delta x}+t_2{}^1\frac{\delta v}{\delta x}+t_3{}^1\frac{\delta w}{\delta x}+t_1{}^2\frac{\delta u}{\delta y}+t_2{}^2\frac{\delta v}{\delta y}+t_3{}^2\frac{\delta w}{\delta y}\right.$$

$$\left.+t_1{}^3\frac{\delta u}{\delta z}+t_2{}^3\frac{\delta v}{\delta z}+t_3{}^3\frac{\delta w}{\delta z}\right)\delta x\,\delta y\,\delta z$$

$$=w_1\,\delta x\,\delta y\,\delta z+w_2\,\delta x\,\delta y\,\delta z.$$

$w_1\,\delta x\,\delta y\,\delta z$ gives the rate at which work is being done on the element in increasing the kinetic energy of the liquid while $w_2\,\delta x\,\delta y\,\delta z$ measures the rate at which work is being done in the deformation of the element. Writing

$$t_j{}^i=-p\delta_j{}^i+2\mu_c d_j{}^i+2\mu_c d_\alpha{}^i d_j{}^\alpha,$$

we see that

$$w_2=(-p+2\mu d_1{}^1+2\mu_c d_\alpha{}^1 d_1{}^\alpha)\frac{\delta u}{\delta x}+(-p+2\mu d_2{}^2$$

$$+2\mu_c d_\alpha{}^2 d_2{}^\alpha)\frac{\delta v}{\delta y}+(-p+2\mu d_3{}^3+2\mu_c d_\alpha{}^3 d_3{}^\alpha)\frac{\delta w}{\delta z}$$

$$+(2\mu d_3{}^2+2\mu_c d_\alpha{}^2 d_3{}^\alpha)(2d_3{}^2)+(2\mu d_1{}^3+2\mu_c d_\alpha{}^3 d_1{}^\alpha)(2d_1{}^3)$$

$$+(2\mu d_2{}^1+2\mu_c d_\alpha{}^1 d_2{}^\alpha)(2d_2{}^1),$$

where the dummy index α, as usual indicates summation. Since

$$d_1{}^1+d_2{}^2+d_3{}^3=\frac{\delta u}{\delta x}+\frac{\delta v}{\delta y}+\frac{\delta w}{\delta z}=0,$$

we may simplify w_2 and finally put it in the form

$$w_2=\mu\{2(d_1{}^1)^2+2(d_2{}^2)^2+2(d_3{}^3)^2+(2d_1{}^3)^2+(2d_2{}^1)^2\}$$

$$+6\mu_c\{d_1{}^1 d_2{}^2 d_3{}^3+2d_2{}^1 d_3{}^2 d_3{}^1-d_1{}^1(d_3{}^2)^2-d_2{}^2(d_3{}^1)^2$$

$$-d_3{}^3(d_2{}^1)^2\}.$$

The coefficient of $6\mu_c$ can be written in the following determinental form.

$$\begin{vmatrix} d_1{}^1 & d_2{}^1 & d_3{}^1 \\ d_1{}^2 & d_2{}^2 & d_3{}^2 \\ d_1{}^3 & d_2{}^3 & d_3{}^3 \end{vmatrix}$$

In the case of plane motion we see again that the cross-viscosity disappears in the expression for w_2 for $d_3{}^1=d_3{}^2=d_3{}^3=0$. The above determinant

is evidently not of a definite sign, unlike the coefficient of μ which is a positive definite quadratic form in the elements d_j^i. Since by its physical nature w_2 cannot be negative, we must have

$$6\,|\,\mu_c\,\{d_1^1 d_2^2 d_3^3 + 2d_2^1 d_3^2 d_3^1 - d_1^1\,(d_3^2)^2 - d_2^2\,(d_3^1)^2 - d_3^3\,(d_2^1)^2\}|$$

$$< \mu\,\{2\,(d_1^1)^2 + 2\,(d_2^2)^2 + 2\,(d_3^3)^2 + (2d_3^2)^2 + (2d_3^1)^2 + (2d_2^1)^2\}.$$

It is worthy of note here that the coefficients of viscosity (μ) and cross-viscosity (μ_c) are not on equal footing, in the analytical or physical sense. In the first place they do not have the same physical dimensions. The features of viscosity and cross-viscosity are indeed quite distinct. While the coefficient of μ in the dissipation term is a positive definite quadratic form in the tensor components d_j^i, the coefficient of μ_c in the same term is a cubic form in the elements d_j^i with no definite sign.

The term $F_2 d_\alpha^i d_j^\alpha$ involving the cross-viscosity $\mu_c = \frac{1}{2}F_2$ has been introduced in the stress-rate of deformation relation (0·5) to explain the hydrodynamical behaviour of highly viscous liquids and the cross-viscosity term ($F_2 d_\alpha^i d_j^\alpha$) in (0·5) may be regarded as a correction to the classical relation (0.3) in the case of ordinary viscous liquids. The dissipation term w_2 should of course always be positive, but this need not be the case for the part of w_2 arising due to cross-viscosity. This forces the conclusion that we cannot conceive of a viscous fluid motion in which the cross-viscosity terms alone are important and the ordinary viscosity terms are neglected.

5. Several interesting questions have been examined in the flow of viscous incompressible fluids by the so-called ' inverse ' and ' semi-inverse ' methods. An investigation of a partial differential equation is called ' inverse ' if the boundary conditions in it are not prescribed at the outset and additional properties of the field (of analytical or geometrical or physical nature) are invoked. An investigation is semi-inverse if *some* of the boundary conditions are prescribed in the beginning, while others are left open, only to be obtained indirectly from simplifying assumptions about the properties of the field.

Some of the major investigations in the case of viscous flows employing the inverse or semi-inverse method deal with problems of a characterizational nature. Thus Jeffery[2] proved that the only steady plane rotational flows of a viscous liquid (in the absence of body forces) for which the isocurls (lines of constant vorticity) coincide with the stream lines of a plane irrotational inviscid flow are those in which only concentric circles or parallel straight lines are admissible as stream lines. The investigations of Jeffery[2]

and Hamel[3] have also shown that the only steady, plane rotational flows of viscous liquids (in the absence of body forces) for which the stream lines coincide with the stream lines of a plane, irrotational inviscid flow are the spiral flows (or their degenerate cases). Problems of this nature require the use of the equations wherein the terms involving pressure have been eliminated.

If such investigations (are to be extended) to the case of a non-Newtonian viscous liquid, one has to start with the equations (2.3). If $\psi(x, y, t)$ denotes the stream function so that the velocity components are

$$u = -\frac{\delta\psi}{\delta y}, \qquad v = \frac{\delta\psi}{\delta x},$$

(2.3) can be put in the form

$$\begin{aligned}
&\frac{\delta}{\delta t}\left(-\frac{\delta\psi}{\delta y}, \frac{\delta\psi}{\delta x}\right) - \left(-\frac{\delta\psi}{\delta y}, \frac{\delta\psi}{\delta x}, 0\right) \times (0, 0, \Delta\psi) \\
&\quad = -\left(\frac{\delta}{\delta x}, \frac{\delta}{\delta y}\right)\left[\Omega + \frac{p}{\rho} + \tfrac{1}{2}\left(\frac{\delta\psi}{\delta x}\right)^2 + \tfrac{1}{2}\left(\frac{\delta\psi}{\delta y}\right)^2\right] \\
&\qquad + \nu\Delta\left(-\frac{\delta\psi}{\delta x}, \frac{\delta\psi}{\delta y}\right) + \tfrac{1}{2}\nu_c\left(\frac{\delta}{\delta x}, \frac{\delta}{\delta y}\right)\left[4\left(\frac{\delta^2\psi}{\delta x\delta y}\right)^2\right. \\
&\qquad \left. + \left(\frac{\delta^2\psi}{\delta x^2} - \frac{\delta^2\psi}{\delta y^2}\right)^2\right]. \qquad (5.1)
\end{aligned}$$

On eliminating the pressure term by cross-differentiation we notice that the cross-viscosity term also drops out as is evident from (2.4) and we have merely

$$\frac{\delta}{\delta t}(\Delta\psi) + \frac{\delta(\psi, \Delta\psi)}{\delta(x, y)} = \nu\Delta\Delta\psi. \qquad (5.2)$$

The first term will not be present in a steady flow. Since this equation does not contain the cross-viscosity coefficient and this is the starting point for all inverse and semi-inverse investigations, we may observe in passing, that such investigations with viscous steady plane flows will not suffer any modifications in the case of non-Newtonian fluids.

5. SUMMARY

The paper deals with some general considerations in the motion of highly viscous liquids for which the stress-rate of deformation relation is $t_j^i = F_0\delta_j^i + F_1 d_j^i + F_2 d_\alpha^i d_j^\alpha$. The equations of motion, the equations

for vorticity and the energy dissipation term are obtained here for a general spatial flow. In the special case of the plane flow, the vorticity equation is free from the cross-viscosity coefficient. This simplifies the study of problems like the addition of two plane motions, consideration of all circulation preserving motions as well as some ' semi-inverse ' investigations in plane motions of non-Newtonian liquids.

6. References

1. Reiner, M. .. "A mathematical theory of dilatancy," *Amer. J. Math.*, 1945, **67**, 350.

2. Jeffery, G. B. .. "On the equations of motion of a viscous fluid," *Phil. Mag.*, 1915, **29**, 445–54.

"On the two-dimensional steady motion of a viscous fluid," *Ibid.*, 1915, **29**, 454–64.

3. Hamel, G. .. "Spiral formige Bewegungen zaher Flussigkeiten," *Jahresberichte der deutschen Mathematiker Vereinigung*, 1916, **25**, 34–60.

CHARACTERISTIC RELATIONS FOR THE ULTRASPHERICAL POLYNOMIALS

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Quite a number of interesting relations have been noticed in recent years (*cf.* the reference at the end of this paper) concerning the ultraspherical (and other orthogonal) polynomials, in connection with the proof of Turán's inequality which had an extraordinary resonance in the recent literature on Special Functions. In the course of proving Turán's inequality for Legendre polynomials, *viz.*,

$$\Delta_n(x) = [P_n(x)]^2 - P_{n+1}(x)\,P_{n-1}(x) \geqslant 0, \quad (n \geqslant 1, \ |x| \leqslant 1), \tag{1}$$

B. S. Madhava Rao and V. R. Thiruvenkatachar[1] established the convexity property of $\Delta_n(x)$ by showing that

$$\frac{d^2}{dx^2}\Delta_n(x) = -\frac{2}{n(n+1)}\left[\frac{d}{dx}P_n(x)\right]^2, \quad (n \geqslant 1). \tag{2}$$

V. R. Thiruvenkatachar and T. S. Nanjundiah[2] employed the formula

$$(1-x^2)\,D_n^{(\lambda)}(x) = \kappa_{n,\lambda}\,\Delta_{n,\lambda}(x) \tag{3}$$

where

$$\Delta_{n,\lambda}(x) = \left(\frac{P_n^{(\lambda)}(x)}{P_n^{(\lambda)}(1)}\right)^2 - \left(\frac{P_{n+1}^{(\lambda)}(x)}{P_{n+1}^{(\lambda)}(1)}\right)\left(\frac{P_{n-1}^{(\lambda)}(x)}{P_{n-1}^{(\lambda)}(1)}\right), \tag{4}$$

$$D_n^{(\lambda)}(x) = \left(\frac{d}{dx}P_n^{(\lambda)}(x)\right)^2 - \frac{d}{dx}P_{n+1}^{(\lambda)}(x)\,\frac{d}{dx}P_{n-1}^{(\lambda)}(x), \tag{5}$$

and

$$\kappa_{n,\lambda} = n(n+2\lambda)\,[P_n^{(\lambda)}(1)]^2$$

for proving Turán's inequality for ultraspherical polynomials $P_n^{(\lambda)}(x)$ in the form

$$\Delta_{n,\lambda}(x) \geqslant 0, \quad (\lambda > -\tfrac{1}{2}, \ n \geqslant 1, \ |x| \leqslant 1). \tag{6}$$

In his work on explicit evaluations of Turán expressions, A. E. Danese[3] has obtained a number of relations which substantially contain the proof

of Turán's inequality for the concerned orthogonal polynomials. K. Venkatachaliengar and the present author[4] have shown that if

$$\Delta_n^{(\lambda)}(x) = [P_n^{(\lambda)}(x)]^2 - P_{n+1}^{(\lambda)}(x)\, P_{n-1}^{(\lambda)}(x),$$

then $\frac{d}{dx} P_n^{(\lambda)}(x)$ can be represented as a numerical multiple of the Wronskian of $P_{n+1}^{(\lambda)}(x)$ and $P_{n-1}^{(\lambda)}(x)$ and have also obtained a series representation of positive functions (apart from a multiplier) for $\frac{d}{dx} \Delta_n^{(\lambda)}(x)$.

The aim of the present note is to point out that these several relations employed or encountered in the course of proving Turán's inequality for $P_n^{(\lambda)}(x)$, are characteristic for the ultraspherical polynomials.

THEOREM 1.—If

$$\Delta_n(x) = [P_n(x)]^2 - P_{n+1}(x)\, P_{n-1}(x), \tag{7}$$

then

$$\frac{d^2}{dx^2} \Delta_n(x) = -\frac{2}{n(n+1)} \left[\frac{d}{dx} P_n(x)\right]^2. \tag{8}$$

This relation is characteristic for Legendre polynomials, *i.e.*, If $\{f_n(x)\}$ is a sequence of polynomials such that the degree of

$$f_n(x) = n; \quad f_0(x) = 1, \quad f_1(x) = x$$

and

$$\frac{d^2}{dx^2} \{[f_n(x)]^2 - f_{n+1}(x) f_{n-1}(x)\} = \frac{-2}{n(n+1)} \left[\frac{d}{dx} f_n(x)\right]^2, \tag{9}$$

then

$$f_n(x) = P_n(x), \quad (n = 0, \ 1, \ 2, \ldots).$$

Proof.—We notice that

$$f_0(x) = P_0(x), \ f_1(x) = P_1(x).$$

Let us assume that

$$f_r(x) = P_r(x), \quad 0 \leqslant r \leqslant n$$

and let

$$f_{n+1}(x) = A_{n+1} x^{n+1} + \ldots.$$

Comparing the coefficients of x^{2n-2} on both sides of (9), we find that

$$A_{n+1} = 2^{n+1} \left|\left(n + \frac{3}{2}\right)\right| \Big/ \left|\left(\tfrac{1}{2}\right)\right| (n+1)!$$

the highest coefficient in $P_{n+1}(x)$, so that we may write

$$f_{n+1}(x) = P_{n+1}(x) + g(x)$$

where $g(x)$ is a polynomial of degree $\leqslant n$. This substitution for $f_{n+1}(x)$ in (9) leads to the equation

$$\frac{d^2}{dx^2}[g(x)\,P_{n-1}(x)] = 0, \qquad (n = 1, 2, 3, \ldots).$$

This second order differential equation has the solution

$$g(x) = (c_1 x + c_2)/P_{n-1}(x), \qquad (n \geqslant 1)$$

which is clearly not compatible with the polynomial nature of $g(x)$. We conclude that $c_1 = c_2 = 0$ or $g(x) = 0$ and thus prove the theorem.

THEOREM 2.—If

$$\Delta_n^{(\lambda)}(x) = [P_n^{(\lambda)}(x)]^2 - P_{n+1}^{(\lambda)}(x)\,P_{n-1}^{(\lambda)}(x) \tag{10}$$

then

$$\frac{d}{dx}\Delta_n^{(\lambda)}(x) = \frac{1-\lambda}{n+\lambda}\begin{vmatrix} P_{n+1}^{(\lambda)}(x) & P_{n-1}^{(\lambda)}(x) \\ \frac{d}{dx}P_{n+1}^{(\lambda)}(x) & \frac{d}{dx}P_{n-1}^{(\lambda)}(x) \end{vmatrix} \tag{11}$$

and the relation is characteristic for the ultraspherical polynomials $P_n^{(\lambda)}(x)$. If $\{f_n^{(\lambda)}(x)\}$ is a sequence of polynomials such that the degree of

$$f_n^{(\lambda)}(x) = n; \quad f_0^{(\lambda)}(x) = 1, \quad f_1^{(\lambda)}(x) = 2\lambda x$$

and

$$\frac{d}{dx}\{[f_n^{(\lambda)}(x)]^2 - f_{n+1}^{(\lambda)}(x)\,f_{n-1}^{(\lambda)}(x)\} \tag{12}$$

$$\frac{1-\lambda}{n+\lambda}\begin{vmatrix} f_{n+1}^{(\lambda)}(x) & f_{n-1}^{(\lambda)}(x) \\ \frac{d}{dx}f_{n+1}^{(\lambda)}(x) & \frac{d}{dx}f_{n-1}^{(\lambda)}(x) \end{vmatrix}$$

then

$$f_n^{(\lambda)}(x) = P_n^{(\lambda)}(x), \quad (n = 0, 1, 2, \ldots).$$

Proof.—We take $\lambda > -\frac{1}{2}$ but omit the case $\lambda = 1$ for then we have $\Delta_n^{(1)}(x) = 1$ and both sides of (11) are zero. As in the proof of Theorem 1, if we take

$$f_r^{(\lambda)}(x) = P_r^{(\lambda)}(x), \; 0 \leqslant r \leqslant n$$

and set

$$f_{n+1}^{(\lambda)}(x) = A_{n+1}^{(\lambda)} x^{n+1} + \ldots,$$

by comparing the highest coefficients in (12), we notice that

$$f_{n+1}^{(\lambda)}(x) = P_{n+1}(x) + g^{(\lambda)}(x),$$

where $g^{(\lambda)}(x)$ is a polynomial of degree $\leqslant n$. Employing this relation in (12) and using (11), we arrive at the relation

$$(n+1)\, g^{(\lambda)}(x) \frac{d}{dx} P_{n-1}^{(\lambda)}(x) + (n + 2\lambda - 1) \frac{dg^{(\lambda)}(x)}{dx} P_{n-1}^{(\lambda)}(x) = 0. \tag{13}$$

We may evaluate $g^{(\lambda)}(x)$ by direct integration. Otherwise, remembering that $P_{n-1}^{(\lambda)}(x)$ and $d/dx\ P_{n-1}^{(\lambda)}(x)$ have no common factor, we conclude from (13) that $g^{(\lambda)}(x) = \alpha P_{n-1}^{(\lambda)}(x)$. It follows then that

$$\alpha\, [(n+1) + (n + 2\lambda - 1)]\, P_{n-1}^{(\lambda)}(x) \frac{d}{dx} P_{n-1}^{(\lambda)}(x) = 0.$$

Thus we are forced to accept that $\alpha = 0$ and the theorem is proved.

THEOREM 3.—The difference equation

$$\frac{d}{dx} \Delta_n^{(\lambda)}(x) = \frac{(n + 2\lambda - 2)(n + 2\lambda - 3)}{n(n+1)} \frac{d}{dx} \Delta_{n-1}^{(\lambda)}(x) - \frac{8(n + \lambda - 1)(1 - \lambda)}{n(n+1)} x\, [P_{n-1}^{(\lambda)}(x)]^2, \tag{14}$$

and the series representation

$$\frac{d}{dx} \Delta_n^{(\lambda)}(x) = \frac{8(\lambda - 1)\, \lfloor n + 2\lambda - 1}{(n+1)!} \times x \sum_{\kappa=1}^{[(n+1)/2]} \frac{(n - 2\kappa + 1)!\, (n - 2\kappa + \lambda + 1)}{\lfloor n - 2\kappa + 2\lambda + 1} \times [P^{(\lambda)}{}_{n-2\kappa+1}(x)]^2 \tag{15}$$

are characteristic relations for the ultraspherical polynomials $P_n^{(\lambda)}(x)$. The proof runs exactly on the same lines as in Theorem 2. Here also, when $\lambda = 1$ both the members of the equation reduce to zero.

THEOREM 4.—The formula

$$(1-x^2)\left\{\left[\frac{d}{dx}\,P_n^{(\lambda)}(x)\right]^2-\frac{d}{dx}\,P_{n+1}^{(\lambda)}(x)\,\frac{d}{dx}\,P_{n-1}^{(\lambda)}(x)\right\}$$
$$=n(n+2\lambda)\,[P_n^{(\lambda)}(x)]^2-(n+1)(n+2\lambda-1)\,P_{n+1}^{(\lambda)}$$
$$\times(x)\,P_{n-1}^{(\lambda)}(x) \tag{16}$$

is characteristic for the ultraspherical polynomials. Here again the proof is as in that of Theorem 2. In the same way we may show that the relation

$$(n+1)(n+2\lambda-1)\{[P_n^{(\lambda)}(x)]^2-P_{n+1}^{(\lambda)}(x)\,P_{n-1}^{(\lambda)}(x)\}$$
$$=4\lambda(1-x^2)\sum_{i=0}^{n-1}\sum_{j=i}^{n-1}\left(\frac{j+\lambda}{j+1}\right)\left(\frac{h_j^{(\lambda)}}{h_i^{(\lambda)}}\right)[P_i^{(\lambda)}(x)]^2$$
$$+(2\lambda-1)\,[P_n^{(\lambda)}(x)]^2,$$

where

$$h_\kappa^{(\lambda)}=(\sqrt{\pi}\,\lfloor\lambda+\tfrac{1}{2}\,\lfloor 2\lambda+\kappa)/(\lfloor 2\lambda\,\lfloor\lambda\,(\kappa+\lambda)\,\kappa!)$$

is characteristic for the ultraspherical polynomials.

REFERENCES

1. Madhava Rao, B. S. and Thiruvenkatachar, V. R. — "On an inequality concerning orthogonal polynomials," *Proc. Ind. Acad. Sci.*, 1949, **29 A**, 391–93.
2. Thiruvenkatachar, V. R. and Nanjundiah, T. S. — "Inequalities concerning Bessel Functions and orthogonal polynomials," *Ibid.*, 1951, **33 A**, 373–84.
3. Danese, A. E. .. — "Explicit evaluations of Turán expressions," *Annali di Mathematica pura ed applicata*, Series, IV, 1955, Tome **38**, 339–48.
4. Venkatachaliengar, K. and Lakshmana Rao, S. K. — "On Turán's inequality for ultraspherical polynomials" (To be published in *Proc. Amer. Math. Society*).

UNIQUENESS OF MAXIMUM PRESSURE FOR THE CUBIC FORM-FUNCTION IN THE GENERAL THEORY OF COMPOSITE CHARGES

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Abstract

In the present paper we have established uniqueness of maximum pressure for composite charges, when each component charge has the cubic form-function. The conditions for the occurrence of maximum pressure in or at the end of any stage have been explicitly obtained.

1. Introduction

To determine the stage or stages of burning in which pressure-maxima can occur and in particular to determine whether the maximum pressure would be unique are important problems from the point of view of designing of guns for use with composite charges. Kapur (1956 *a*, *b*) established the uniqueness of maximum pressure under the following assumptions:

(*i*) rate of burning proportional to pressure for each component charge.

(*ii*) $\gamma_1 = \gamma_2 = \ldots\ldots = \gamma_n$

(*iii*) Specific volume = Co-volume for each component charge.

(*iv*) the standard quadratic form-function of the type

$$z = (1 - f)(1 + \theta f) \tag{1}$$

for each component charge.

The first two are the usual assumptions. The effect of taking co-volume-correction terms has been examined in a recent paper [Kapur (1957)], where it has been proved that except for very highly progressive forms obtained by inhibiting certain surfaces from burning—forms which are used in rockets but not in guns—the uniqueness of maximum pressure holds even when we take these co-volume-correction terms into account. As for assumption (*iv*), most of the forms used in practice can be more correctly expressed by the cubic form-function

$$z = (1 - f)(1 + \theta f + \psi f^2) \tag{2}$$

Since in most of the common forms, tube, cord, ribbon, flake, ψ is small and positive, form (1) is preferred for analytical solutions, specially because form (2) gives rise to complicated solutions. It is however desirable to establish the uniqueness theorem under as general conditions as possible and fortunately we find, that the proof, while deeper, is not more complicated for the cubic form-function. We have also to remember that for highly degressive shapes like spheres ψ can be as high as unity. ψ can also be negative for inhibited charges, but such shapes are not used in guns and consequently we shall assume ψ to be positive in our discussions. The method used here to establish the uniqueness of maximum pressure for the cubic form-function is the Equivalent Charge Method of Corner (1950) and Clemmow (1951) as improved by Kapur (1956 *c*).

2. The Basic Equations for the Equivalent Charge

Let F_i, C_i, D_i, β_i, z_i, f_i, θ_i, ψ_i refer to the ith component charge, and let F, C, D, B, z, f, θ, ψ refer to the equivalent charge, then the fundamental equations for the equivalent charge [Kapur (1956 *c*, 1957)] are:

$$FCz = Ap\,(x + l) + \tfrac{1}{2}(\gamma - 1)\, w_1 v^2 \tag{3}$$

$$D\frac{df}{dt} = -\beta p. \tag{4}$$

$$w_1 v\frac{dv}{dx} = w_1\frac{dv}{dt} = Ap \tag{5}$$

$$z = A_r + B_r(1 - f) - E_r(1 - f)^2 + D_r(1 - f)^3 \tag{6}$$

when

$$1 - \frac{1}{k_{r-1}} \geqslant f \geqslant 1 - \frac{1}{k_r}, \tag{6 a}$$

where

$$A_r = \sum_{i=1}^{r-1} \lambda_i \tag{7 a}$$

$$B_r = \sum_{i=r}^{n} \lambda_i k_i (1 + \theta_i + \psi_i), \tag{7 b}$$

$$E_r = \sum_{i=r}^{n} \lambda_i k_i^2 (\theta_i + 2\psi_i), \tag{7 c}$$

$$D_r = \sum_{i=r}^{n} \lambda_i k_i^3 \psi_i \tag{7 d}$$

and

$$\lambda_i = \frac{F_i C_i}{\sum_{i=1}^{n} F_i C_i} = \frac{F_i C_i}{FC} \tag{8}$$

$$k_i = \frac{\beta_i'}{\beta'} = \frac{\beta_i/D_i}{\beta/D} = \frac{\beta_i/D_i}{\beta_n/D_n'} \tag{9}$$

and charges have been so numbered that

$$\beta_1' \geqslant \beta_2' \geqslant \ldots\ldots\ldots\ldots\ldots\ldots \geqslant \beta_n' \tag{10}$$

Using (4) and (6), we get

$$v = \frac{AD}{\beta w_1}(f_0 - f), \tag{11}$$

where f_0 is value of f at shot-start.

From (3), (4), (5), (6) and (11), we get

$$\frac{A(x+l)}{FC}\frac{dp}{df} = -B_r + 2E_r(1-f) - 3D_r(1-f)^2 + \gamma M(f_0 - f), \tag{12}$$

where

$$M = \frac{A^2D^2}{\beta^2 w_1 FC} \tag{13}$$

is the central ballistic parameter for the equivalent charge.

Also from the equations of the rate of burning

$$\frac{D_r}{\beta_r}\frac{df_r}{dt} = \frac{D}{\beta}\frac{df}{dt} = -p$$

$$\therefore \quad \frac{1-f_r}{\beta_r'} = \frac{1-f}{\beta'}$$

or

$$1 - f = \frac{1}{k_r}(1 - f_r) \tag{14}$$

Using (14), we can write (12) as

$$\frac{A(x+l)}{FC}\frac{dp}{df} = -\left[\frac{3D_r}{k_r^2}f_r^2 + \frac{f_r}{k_r}\left(\gamma M + 2E_r - \frac{6D_r}{k_r}\right) + \left(B_r - \frac{2E_r}{k_r} + \frac{3D_r}{k_r^2} - \frac{\gamma M}{k_r} + \gamma M(1-f_0)\right)\right] \tag{15}$$

3. Discontinuity of dp/df at the End of a Stage

At the end of the r-th stage, $f = 1 - 1/k_r$ and therefore from (12)

$$\frac{dp}{df} = \frac{FC}{A(x_r+l)}\left[-B_r + \frac{2E_r}{k_r} - \frac{3D_r}{k_r^2} + \frac{\gamma M}{k_r} - \gamma M(1-f_0)\right] \tag{16}$$

where x_r is the shot-travel till the end of the r-th stage.

Similarly at the beginning of the $(r+1)$th stage

$$\frac{dp}{df} = \frac{FC}{A(x_r+l)}\left[-B_{r+1} + \frac{2E_{r+1}}{k_r} - \frac{3D_{r+1}}{k_r^2} + \frac{\gamma M}{k_r} - \gamma M(1-f_0)\right] \tag{17}$$

therefore increment in dp/df at the end of the r-th stage

$$= \frac{FC}{A(x_r+l)}\left[-(B_{r+1}-B_r) + \frac{2}{k_r}(E_{r+1}-E_r) - \frac{3}{k_r^2} \times (D_{r+1}-D_r)\right]$$

$$= \frac{FC}{A(x_r+l)}\lambda_r k_r(1-\theta_r) \tag{18}$$

Now if

$$z = (1-f)(1+\theta_r f + \psi_r f^2) \tag{19}$$

is to represent a form-function for a charge, dz/df should be negative for all values of f lying between 0 and 1, though it may vanish at $f=0$ and $f=1$. From this fact, we easily deduce

$$(i) \qquad 1-\theta_r \geqslant 0 \tag{20 a}$$

$$(ii) \quad 1+\theta_r+\psi_r \geqslant 0. \tag{20 b}$$

From (18) and (20 a), we find that in crossing from the r-th stage to the $(r+1)$th, dp/df always receives a non-negative increment. Therefore

if dp/df is negative at the end of a stage, it can become positive at the beginning of the next; but if dp/df is positive at the end of the previous stage, it cannot become negative at the beginning of the next.

4. Uniqueness of Maximum Pressure

We shall establish the uniqueness for the case when

$$\psi_1 > 0, \ \psi_2 > 0, \ldots\ldots, \ \psi_n > 0 \tag{21 a}$$

$$\theta_1 \geqslant \psi_1, \ \theta_2 \geqslant \psi_2, \ldots\ldots, \ \theta_n \geqslant \psi_n \tag{21 b}$$

These conditions are satisfied by most charges used in practice, as is shown by the following *table*:

Charge	Cord	Tube	Sphere	Cube	Ribbon	Square-flake
θ	1	$1/\lambda$	1	1	$1/\lambda+1/\mu-1/\lambda\mu$	$2/\mu-1/\mu^2$
ψ	$1/\lambda$	0	1	1	$1/\lambda\mu$	$1/\mu^2$

Here λ and μ are large and are above 100 for service propellants.

For this case $\theta_r > 0$ for all r, and from (7), A_r, B_r, E_r, D_r, are positive for all r. Also

$$\begin{aligned}\gamma M + 2E_r - \frac{6D_r}{k_r} &= \gamma M + 2\sum_{i=r}^{n} \lambda_i k_i^2 \left[\theta_i + 2\psi_i - \frac{3k_i}{k_r}\psi_i\right] \\ &= \gamma M + 2\sum_{i=r}^{n} \lambda_i k_i^2 \left[(\theta_i - \psi_i) + 3\psi_i\left(1 - \frac{k_i}{k_r}\right)\right]\end{aligned} \tag{22}$$

Since

$$k_i \leqslant k_r \quad \text{for} \quad r \geqslant n,$$

we find from (21) and (22) that

$$\gamma M + 2E_r - \frac{6D_r}{k_r} > 0 \quad \text{for all} \quad r.$$

Now let

$$K_r \equiv B_r - \frac{2E_r}{k_r} + \frac{3D_r}{k_r^2} - \frac{\gamma M}{k_r} + \gamma M (1 - f_0), \tag{23}$$

then (15) shows that

(*i*) If $K_r > 0$, dp/df does not vanish in the r-th stage, and pressure continues to increase steadily in this stage.

(*ii*) If $K_r = 0$, dp/df can vanish for a negative value of f_r (which is inadmissible) and for $f_r = 0$ (*i.e.*, at the end of the r-th stage).

(*iii*) If $K_r < 0$, dp/df can vanish for two values of f_r. One of these is negative and therefore inadmissible. The other is positive and would be admissible if it is less than unity.

Thus dp/df can vanish at most once during a stage and a pressure maximum or minimum can arise at this instant. However (15) shows that since D_r and $\gamma M + 2E_r - 6D_r/k_r$ are positive and since f_r has some positive value at the beginning of the r-th stage and is zero at its end, the negative contribution to dp/df is reduced during the r-th stage, and therefore if dp/df is negative at the beginning of the r-th stage, it can become positive at its end and not *vice-versa*. Consequently only a pressure maximum can arise during a stage.

At the end of a stage also, since dp/df receives a non-negative increment, it can change there from negative to positive and not *vice-versa*, and thus a pressure maximum can occur there, but a pressure minimum cannot occur there.

Thus we find that both during a stage and at the end of a stage, dp/df can change only from negative to positive (or zero) and consequently once dp/df has become positive, it cannot become negative again. The uniqueness of maximum pressure is thus established.

5. Conditions for the Occurrence of Maximum Pressure in or at the End of any Stage

The maximum pressure would occur in the r-th stage if dp/df is negative at the beginning of this stage and positive at its end. The corresponding conditions are, from (12):

$$-B_r + \frac{2E_r}{k_{r-1}} - \frac{3D_r}{k^2_{r-1}} + \frac{\gamma M}{k_{r-1}} - \gamma M(1 - f_0) < 0 \qquad (24\,a)$$

and

$$-B_r + \frac{2E_r}{k_r} - \frac{3D_r}{k_r^2} + \frac{\gamma M}{k_r} - \gamma M(1 - f_0) > 0. \qquad (24\,b)$$

The maximum pressure would occur at the end of the r-th stage if

(*i*) dp/df is negative at the end of the r-th stage and positive at the beginning of the $(r+1)$th, or

(*ii*) dp/df is zero at the end of the r-th stage, or

(*iii*) dp/df is zero at the beginning of the $(r+1)$th stage.

The corresponding conditions are:

$$(i) \qquad -B_r + \frac{2E_r}{k_r} - \frac{3D_r}{k_r^2} + \frac{\gamma M}{k_r} - \gamma M(1-f_0) < 0 \qquad (25\,a)$$

and

$$-B_{r+1} + \frac{2E_{r+1}}{k_r} - \frac{3D_{r+1}}{k_r^2} + \frac{\gamma M}{k_r} - \gamma M(1-f_0) > 0 \qquad (25\,b)$$

or

$$(ii) \qquad -B_r + \frac{2E_r}{k_r} - \frac{3D_r}{k_r^2} + \frac{\gamma M}{k_r} - \gamma M(1-f_0) = 0 \qquad (25\,c)$$

or

$$(iii) \qquad -B_{r+1} + \frac{2E_{r+1}}{k_r} - \frac{3D_{r+1}}{k_r^2} + \frac{\gamma M}{k_r} - \gamma M(1-f_0) = 0. \qquad (25\,d)$$

The maximum pressure would occur at all-burnt if

$$-B_n + \frac{2E_n}{k_n} - \frac{3D_n}{k_n^2} + \frac{\gamma M}{k_n} - \gamma M(1-f_0) \leqslant 0.$$

Remembering that $k_n = 1$ and using (7), this simplifies to

$$\lambda_n(1-\theta_n) \geqslant \gamma M f_0. \qquad (26)$$

When $\psi_1 = \psi_2 = \ldots = \psi_n = 0$, so that $D_r = 0$ for all r, the conditions (24), (25) and (26) reduce to the corresponding conditions for the standard quadratic form-function [Kapur (1956 *b*)].

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REFERENCES

1. Clemmow, C. A. .. *Chapter XI, Internal Ballistics H.M.S.O.*, London, 1951.
2. Corner, J. .. *Interior Ballistics of Guns*, New York, 1950.
3. Kapur, J. N. .. "Uniqueness of Maximum Pressure in the General Theory of Composite Charges," *Proc. Nat. Inst. Sci.*, 1956 *a*, **22 A**, 236–255.
4. ———— .. "Uniqueness of Maximum Pressure for orthodox, H/L and R.C.L. guns by the Equivalent Charge Method," *Proc. 1st Cong. Th. App. Mech.*, 1956 *b*, **1**, 227–38.
5. ———— .. "Equivalent Charge Method in the General Theory of Composite Charge," *Proc. Nat. Inst. Sci.*, 1956 *c*, **22 A**, 63–81.
6. ———— .. "General Theory of Composite Charges," *Mem. artellerie franc*, 1957 (in press).

POLAROGRAPHIC BEHAVIOUR OF METALS IN ETHANOLAMINES

Part III. Nickel

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Introduction

Jessop[1] has reported that in alkaline triethanolamine solutions nickel gives a wave of poor shape. Preliminary investigations in this laboratory indicated that the use of ethanolamines under varying conditions produced waves which could be of great help in the polarographic estimation of nickel. Consequently, a detailed investigation of the polarography of nickel was undertaken and the results obtained are reported below.

Experimental

The polarograms have been recorded automatically by the Cambridge Instrument Company polarograph. The procedure and other experimental details are substantially the same as those described previously.[2] The drop-time of the capillary has been 5 seconds in 1 N potassium chloride and the value of $m = 1 \cdot 150$ mg. per second. The temperature of recording the polarograms has been $30^\circ \pm 0 \cdot 1^\circ$ C.

Results

1. *Effect of pH*

In these experiments, the concentration of the amine was kept at 0·1 M, and that of nickel at 1·6 millimolar. Gelatin (0·005%) was employed to suppress the maxima which appear in the solutions containing mono- and diethanolamines. Since the solubility of the complex in 0·1 M solutions is low, slight precipitation occurs at about pH 10. It is surprising that at pH 11, both in mono- and in diethanolamines, maxima persist even after the addition of gelatin under the above conditions. Table I presents the results of analysis of the waves.

TABLE I

Effect of pH on the polarographic behaviour of nickel in presence of ethanolamines

Amine used	pH	Half-wave potential $E_{\frac{1}{2}}$ *vs.* S.C.E. (Volt)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (Volt)
Monoethanolamine..	6·50	−1·038	0·108
	9·20	−0·862	0·042
	11·00	Maximum not suppressed	
	12·70	−0·986	0·029
	13·50	−1·043	0·029
Diethanolamine ..	6·05	−1·069	0·116
	9·00	−0·933	0·064
	10·70	Maximum not suppressed	
	12·70	−1·163	0·048
	13·50	Split waves	
Triethanolamine ..	5·60	−1·093	0·099
	7·20	−1·100	0·087
		−1·248	
	8·65	−1·065	0·076
		−1·196	0·038
	9·70	−1·090	0·065
		−1·207	0·034
	12·70	−1·240	0·074
		−1·386	
	13·50	−1·292	0·068
		−1·490	
		−1·680	

A perusal of the table indicates that the reduction process is irreversible in most cases except in alkaline monoethanolamine solutions. The phenomenon of "split-wave" which is absent in monoethanolamine, becomes noticeable only in highly alkaline diethanolamine solutions whereas in triethanolamine solutions it starts from a pH 7·20. The complexity of the wave in alkaline triethanolamine solution can be seen from Fig. 1.

2. *Effect of Variation of the Composition of the Base Electrolyte*

During the present studies noteworthy features of complex formation have been revealed only in alkaline region as in the case of cadmium.[3] The results obtained with solutions of sodium hydroxide, sodium carbonate and ammonium chloride-ammonium hydroxide are presented below.

(*i*) *Sodium hydroxide*.—The polarograms in Figs. 1 and 2 show the effect of sodium hydroxide on the behaviour of nickel in presence of ethanolamines,

where 0·005% gelatin has been employed to suppress the maxima in solutions containing mono- and diethanolamines. As we go from mono- to triethanaolamine (Table II) it is evident that a single reduction wave gives

TABLE II

Effect of sodium hydroxide on the polarographic behaviour of nickel in presence of ethanolamines

Concentration of nickel: 1·60 millimolar

Amine used	Concentration of		Half-wave potential $E_{\frac{1}{2}}$ *vs.* S.C.E.	$E_{\frac{1}{4}} - E_{\frac{1}{2}}$	Wave height at *s*/30
	Amine (Molar)	Sodium hydroxide (Molar)	(Volt)	(Volt)	
Monoethanolamine	0·50	0·10	−1·028	0·030	45·1*
	1·00	0·10	−1·045	0·028	46·3
	0·50	1·00	−1·084	0·033	38·7
	1·00	1·00	−1·102	0·034	40·8
Diethanolamine ..	0·30	0·10	−1·097	0·048	41·7
	0·65	0·10	−1·125	0·050	40·9
	1·00	0·10	−1·138	0·045	39·1
	0·30	1·00	−1·150	Irreversible	35·3*
			−1·210	waves. Mea-	
	0·65	1·00	−1·270	surement	36·6
			−1·380	difficult	
	1·00	1·00	−1·380		34·1
			−1·490		
Triethanolamine ..	0·10	0·10	−1·240	0·074	37·5*
			−1·390		
	0·30	0·10	−1·280	0·048	40·7
			−1·420		
	0·60	0·10	−1·320	0·057	36·8
			−1·500		
	1·00	0·10	−1·330	0·063	34·2
			−1·510		
	0·10	1·00	−1·292	0·068	Measurement
			−1·500		difficult
			−1·670		
	0·30	1·00	−1·333	0·061	,,
			−1·540		
			−1·690		
	0·60	1·00	−1·365	0·071	,,
			−1·530		
			−1·740		
	1·00	1·00	−1·385	0·068	,,
			−1·550		

* Values are approximate.

place to ill-separated reduction steps of two or three different species in sluggish equilibrium.[3] It is clear from the table that reduction proceeds reversibly in monoethanolamine, while in di- and triethanolamines, the reduction process is irreversible. These results are in contrast to the results obtained with cadmium,[3] where the complexes of diethanolamine and of monoethanolamine showed greater similarity.

(*ii*) *Sodium carbonate.*—In Fig. 3 are given polarograms of nickel in monoethanolamine. Curves in di- and triethanolamines are similar to those in monoethanolamine. Gelatin (0·005%) is added to the base solutions containing mono- and diethanolamines to act as the maximum suppressor. Table III gives the half-wave potentials and the values of $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ for the systems studied.

The results given in Table III indicate that the reduction of the monoethanolamine complex proceeds very nearly reversibly while in di- and tri-

TABLE III

Effect of sodium carbonate on the polarographic behaviour of nickel in presence of ethanolamines

Concentration of nickel: 1·60 millimolar.

Amine used	Concentration of		Half-wave potential $E_{\frac{3}{4}}$ *vs.* S.C.E.	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$	Height of the wave $s/50$
	Amine (Molar)	Sodium carbonate (Molar)	(Volt)	(Volt)	
Monoethanolamine	0·30	0·10	−0·974	0·034	49·2
	0·65	0·10	−1·001	0·032	47·6
	1·00	0·10	−1·018	0·033	46·0
	0·30	1·00	−1·000	0·034	39·0
	0·65	1·00	−1·022	0·032	37·0
	1·00	1·00	−1·043	0·033	36·1
Diethanolamine ..	0·30	0·10	−1·031	0·068	44·4
	0·65	0·10	−1·060	0·064	41·5
	1·00	0·10	−1·076	0·068	39·6
	0·30	1·00	−1·089	0·076	34·9
	0·65	1·00	−1·121	0·069	32·5
	1·00	1·00	−1·134	0·064	30·4
Triethanolamine ..	0·02	0·10	−1·088	0·095	Precipitation
	0·10	0·10	−1·190	0·088	42·5
	1·00	0·10	−1·290	0·068	34·2

ethanolamine solutions the reduction process is irreversible in character. Even in sodium carbonate solutions, the nickel-diethanolamine complex resembles the triethanolamine complex, thus differing substantially from cadmium[3] complexes.

(*iii*) *Ammonium chloride* (1 *M*) *and ammonium hydroxide* (1 *M*).—The effect of ammonium chloride-ammonium hydroxide mixture is given in Table IV.

TABLE IV

Effect of ammonium chloride (1 *M*)*—ammonium hydroxide* (1 *M*) *on the polarographic behaviour of nickel in presence of ethanolamines*

Concentration of nickel: 1·60 millimolar.

Amine used	Concentration of amine (Molar)	Half-wave potential $E_{\frac{1}{2}}$ *vs.* S.C.E. (Volt)	$E_{\frac{1}{4}} - E_{\frac{1}{2}}$ (Volt)	Height of the wave at *s*/50
Monoethanolamine ..	0·10	−1·066	0·059	63·2
	0·50	−1·081	0·056	62·4
		−1·226		
	1·00	−1·092	0·052	59·8
		−1·275		
Diethanolamine ..	0·10	−1·070	0·069	62·3
	0·50	−1·097	0·063	58·9
	1·00	−1·114	0·064	55·5
Triethanolamine ..	0·10	−1·080	0·062	57·7
	0·30	−1·132	0·077	55·9
	0·60	−1·173	0·098	52·4
	1·00	−1·189	0·104	47·9

It is clear that the reduction proceeds irreversibly in all the cases. With mono- and diethanolamines the irreversibility is almost constant between 0·1 and 1·0 M concentration of the amine, while in the case of triethanolamine it increases with increasing concentration of the amine and becomes almost constant when the concentration of the amine is increased beyond 0·6 M.

In the case of monoethanolamine another small wave appears at − 1·23 V *vs.* S.C.E. in 0·5 M solution. This value increases to ca. − 1·28 V *vs.* S.C.E. in 1 M solution. With diethanolamine, however, the bend before the diffu-

sion current plateau is pressed inside. Triethanolamine complex, on the other hand, does not show such phenomenon.

3. *Effect of Concentration of Nickel on the Diffusion Current Constant in Presence of Sodium Hydroxide, Sodium Carbonate and Ammonium Chloride-Ammonium Hydroxide*

The results obtained are given in Table V. The effect of concentration of nickel on the diffusion current constant has not been tested in the case

TABLE V

*Effect of concentration of nickel on the diffusion current constant**

Concentration of the amine: 1 M

Concentration of nickel (Millimolar)	Diffusion current constant $\frac{i_d}{Cm^{\frac{2}{3}} t^{\frac{1}{6}}}$	Concentration of nickel (Millimolar)	Diffusion current constant $\frac{i_d}{Cm^{\frac{2}{3}} t^{\frac{1}{6}}}$
(1) *B.S.:* 1·00 *M Moen*+0·10 *M NaOH* + 0·025% gelatin		(5) *B.S.:* 1·00 *M Moen*+0·10 *M* Na_2CO_3 + 0·025% *gelatin*	
$X = 1·415$ *at* $-1·30$ *V vs. S.C.E.*		$X = 1·424$ *at* $-1·30$ *V vs. S.C.E.*	
1·600	2·83	1·600	2·99
8·000	2·80	8·000	3·01
(2) *B.S.:* 1·00 *M Dien*+0·10 *M NaOH* + 0·025% *gelatin*		16·00	2·93
$X = 1·408$ *at* $-1·40$ *V vs. S.C.E.*		(6) *B.S.:* 1·00 *M Moen*+1·00 *M* Na_2CO_3 + 0·025% *gelatin*	
1·600	2·37	$X = 1·424$ *at* $-1·30$ *V vs. S.C.E.*	
8·000	2·35	1·600	2·34
(3) *B.S.:* 1·00 *M Dien*+1·00 *M NaOH* +0·005% *gelatin*		8·000	2·32
$X = 1·408$ *at* $-1·40$ *V vs. S.C.E.*		16·000	2·32
1·600	2·32	(7) *B.S.:* 1·00 *M Dien*+0·10 *M* Na_2CO_3 + 0·025% *gelatin*	
8·000	2·30	$X = 1·424$ *at* $-1·30$ *V vs. S.C.E.*	
(4) *B.S.:* 1·00 *M Trien*+0·10 *M NaOH*		1·600	2·16
$X = 1·373$ *at* $-1·60$ *V vs. S.C.E.*		8·000	2·14
1·600	2·46	(8) *B.S.:* 1·00 *M Dien*+1·00 *M* Na_2CO_3 + 0·005% *gelatin*	
3·200	2·44	$X = 1·424$ *at* $-1·30$ *V vs. S.C.E.*	
8·000	2·44	1·600	2·04
		8·000	2·03
		(9) *B.S.:* 1·00 *M Trien*+0·10 *M* Na_2CO_3	
		$X = 1·383$ *at* $-1·60$ *V vs. S.C.E.*	
		1·600	2·44
		3·200	2·46
		8·000	2·43

*Abbreviations:–B.S.–Base solution; X–$m^{\frac{2}{3}} t^{\frac{1}{6}}$ in $mg^{\frac{2}{3}}$ $sec^{-\frac{1}{2}}$ Moen–monoethanolamine; Dien–diethanolamine; Trien–triethanolamine.

of ammonium chloride and ammonium hydroxide since nickel is quite soluble in ammonium hydroxide-ammonium chloride and the incorporation of ethanolamines does not in any way help in the practical estimation of the metal. In solutions containing sodium hydroxide, 1 molar amine is incorporated in the base solution since the nickel complex is not sufficiently soluble at lower concentrations of the amine. Since in certain base solutions maximum appeared at higher concentration of nickel when 0·005% gelatin is used, the concentration of gelatin has been increased to 0·025%, though this brings about a decrease of the diffusion current by nearly 12%. In triethanolamine solutions, normal sodium hydroxide gives rise to waves of poor shape, while in the case of monoethanolamine solutions the nickel gets precipitated due to the low solubility of the complex. Hence it can be concluded that the use of 1 M sodium hydroxide in base solutions is not suitable for analytical estimation of the metal. As in the case of sodium hydroxide 0·025% gelatin had to be employed to prevent the appearance of maxima at higher concentration of nickel in some of the base solutions. From the results it can be concluded that in sodium carbonate solutions also, nickel can be estimated in all the three ethanolamines. The use of monoethanolamine has a decided advantage over di- and triethanolamines as the reduction process is reversible and the value of diffusion current constant is greater than in the other two amines.

DISCUSSION

1. *Splitting of the Polarographic Wave in Triethanolamine*

The splitting up of the polarographic wave is quite prominent in sodium hydroxide solutions (Fig. 1). The main wave in each of the polarograms is due to the complex containing the amine and hydroxyl while the other two are due to complexes containing more of the hydroxyl in sluggish equilibrium, analogous to the complexes of cadmium[3] studied by the present author. Of the ill-separated doublets that appear between pH 10 and 7, the first corresponds to the reduction of aquonickel ion as its half-wave potential is found to be $-1{\cdot}06$ V and the second corresponds to a complex of the amine (Table I).

2. *Splitting of the Polarographic Wave in Mono- and Diethanolamines*

In contrast to the behaviour of triethanolamine, splitting is practically absent in monoethanolamine solutions. However, the small second wave that appears with ammonium chloride-ammonium hydroxide solutions is presumably due to a species of the complex, containing more of the amine than of the complex giving rise to the main wave. Similar explanations can also be given for the elongated bend with the diethanolamine solutions.

The diethanolamine solutions show the splitting in 1·0 M sodium hydroxide solutions. In this case also it is reasonable to expect the second species, to contain more of the hydroxyl groups.

3. *Effect of pH*

Mono-and diethanolamines.—In acid solutions (pH ca. 6) the half-wave potential is of the order of − 1·04 V *vs.* S.C.E. and the wave is highly irreversible the value of $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ being of the order of 0·100 V (*vide* Table I) as compared to a value of 0·029 V required by a reversible two-electron reduction process. The half-wave potential of hexa-aquonickel ion is ca. − 1·10 V *vs.* S.C.E. and the wave is irreversible. It therefore appears that in acid solutions it is the aquonickel ion that is getting reduced. When the pH is increased, the half-wave potential and the value of $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ drops. This indicates complex formation as it is known[4] that nickel is more reversibly reduced in presence of complexing agents. At lower pH values in the alkaline range there is complex formation with amine but as the concentration of the hydroxyl group becomes high as compared to the concentration of the nickel, hydroxyl group also enters the complex.

4. *Nature of Complex Formation in Sodium Hydroxide Solutions*

(*i*) *Monoethanolamine.*—In monoethanolamine solutions reduction occurs nearly reversibly. Applying Lingane's[3] equation the formula for the complex is obtained as $Ni\,(Moen)_2\,(OH)_2$.

(*ii*) *Diethanolamine.*—In this case the reduction process is irreversible. Applying equations for irreversible waves[2] one gets that one molecule of diethanolamine enters at lower concentrations of the amine and two molecules at higher concentrations of the amine.

(*iii*) *Triethanolamine.*—With triethanolamine solutions the irreversibility of the main wave does not alter much with the change in the concentration of the amine in solutions containing 1 M sodium hydroxide. Application of equations for irreversible waves[2] indicates that one molecule of the triethanolamine has entered the complex.

5. *Nature of Complex Formation in Sodium Carbonate Solutions*

(*i*) *Monoethanolamine.*—When monoethanolamine is used in the base solution, the reduction process is nearly reversible. From the data presented in Table III it is clear that one carbonate group has entered in the complex. Depending upon the concentration of the amine 2, 3 or 4 molecules of the amine enter the complex. The composition of the complexes can be written as follows: $Ni\,(Moen)_2\,(CO_3)_1$, $Ni\,(Moen)_3\,(CO_3)_1$, $Ni\,(Moen)_4\,(CO_3)_1$.

(*ii*) *Diethanolamine.*—The polarographic waves are irreversible in nature. It can be concluded by application of equations for irreversible waves[2] that one molecule of the amine and one $CO_3^{=}$ group enters the complex. The formula can be written as follows: $Ni(Dien)_1(CO_3)_1$.

(*iii*) *Triethanolamine.*—It was not possible to derive any conclusions regarding the nature of the complex due to progressive change of irreversibility with the complexing agent.

6. *Nature of Complex Formation in Presence of Ammonium Chloride-Ammonium Hydroxide*

That ethanolamines have entered into the complex is indicated by the shift in the half-wave potential. It can be concluded by the application of equations for irreversible waves[2] to the data presented in Table IV to the concentration range where irreversibility is a constant, it is found that one molecule of the amine enters the complex.

7. *Irreversibility of Polarographic Waves*

In the case of nickel both the di- and triethanolamines give irreversible polarographic waves in contradistinction to the behaviour of cadmium,[3] where only the triethanolamine complexes give irreversible waves.

To explain the irreversibility of the reduction process in the case of triethanolamine complexes of cadmium,[3] it has been suggested that the presence of three hydroxyl groups in triethanolamine may be responsible to make the reduction process activation-controlled.

In the case of nickel, however, the gradation of the three types of complexes is marked, the degree of irreversibility depending upon the number of ethanol groups in the amine.

In the case of monoethanolamine, the reduction process is reversible. In base solutions containing ammonium chloride-ammonium hydroxide, there is a slight irreversibility. This may be due to the presence of ammonia in the complex. In the case of di- and triethanolamines, the reduction processes are irreversible, the degree of irreversibility being much greater with triethanolamine complexes.

8. *Height of the Polarographic Wave and the Number of Ethanol Groups in the Amine*

Reference to Tables II, III and IV indicates that the height of the polarographic wave decreases with an increase in the number of ethanol groups indicating a decrease in the diffusion coefficient.

9. *Thermodynamic Data from Polarographic Measurements*

The reversible half-wave potential of nickel ion is not known since the reduction of the simple nickel ion proceeds irreversibly. It has not been possible to calculate the hypothetical reversible half-wave potential from the dissociation constant data of the ammonia complexes as the reduction of these complexes do not proceed reversibly at the dropping mercury electrode. Consequently, the conclusions arrived at will not be quite accurate.

In conclusion, it can be stated that the polarographic investigations recorded in the present paper reveal the formation of the following complexes containing the ethanolamines:

$Ni(Moen)_2(OH)_2$	$Ni(Moen)_2(CO_3)_1$	$Ni(Moen)_3(CO_3)_1$
$Ni(Moen)_4(CO_3)_1$	$Ni(Moen)_1(NH_3)_x^{++}$	$Ni(Dien)_1(OH)_y^{2-y}$
$Ni(Dien)_2(OH)_z^{2-z}$	$Ni(Dien)_1(CO_3)_1$	$Ni(Dien)_1(NH_3)_y^{++}$
$Ni(Trien)_1(OH)_z^{2-z}$	$Ni(Trien)_1(NH_3)_z^{++}$	

SUMMARY

1. The polarographic behaviour of nickel has been studied in all the three ethanolamines at various pH values and in the following alkaline reagents: (1) sodium hydroxide, (2) sodium carbonate, (3) ammonium chloride-ammonium hydroxide.

2. The reduction process is essentially irreversible at all pH values except in alkaline monoethanolamine solutions.

3. The phenomenon of "split-wave" is very prominent in triethanolamine solutions above pH 7, and in highly alkaline diethanolamine solutions. An explanation based on the sluggish equilibrium between different species of complexes has been put forward.

4. Evidence is presented for the existence of the following complexes based on polarographic data:

$Ni(Moen)_2(OH)_2$	$Ni(Moen)_2(CO_3)_1$	$Ni(Moen)_3(CO_3)_1$
$Ni(Moen)_4(CO_3)_1$	$Ni(Moen)_1(NH_3)_x^{++}$	$Ni(Dien)_1(OH)_y^{2-y}$
$Ni(Dien)_2(OH)_z^{2-z}$	$Ni(Dien)_1(CO_3)_1$	$Ni(Dien)_1(NH_3)_y^{++}$
$Ni(Trien)_1(OH)_z^{2-z}$	$Ni(Trien)_1(NH_3)_z^{++}$	

5. Polarographic determinations of nickel can be made taking advantage of the reduction of the ethanolamine complexes.

6. Difficulties in calculating the thermodynamic constants from polarographic data even in the case of reversible systems, have been pointed out.

ACKNOWLEDGEMENT

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REFERENCES

1. Jessop, G. .. *Nature*, 1946, **158**, 59.
2. Subrahmanya, R. S. .. *Proc. Indian Acad. Sci.*, 1956, **43 A**, 133.
3. ———— .. *Ibid.*, 1956, **43 A**, 383.
4. Kolthoff, I. M. and Lingane, J. J. *Polarography*, 1952, **2**, 486, Interscience Publishers, New York.

EXPLANATION OF PLATES

FIG. 1. Effect of sodium hydroxide (1·0 M) on the polarographic behaviour of nickel (1·600 millimolar) in triethanolamine.

Curves 1 to 5 have been taken using 0·02, 0·10, 0·30, 0·60 and 1·00 M triethanolamine respectively. There was partial precipitation under the conditions in which Curve 1 was recorded.

Sensitivity: *s*/15 for Curve 1 and *s*/50 for Curves 2 to 5.

The voltage line just preceding each polarogram corresponds to − 1·073 V *vs.* S.C.E.

FIG. 2. Effect of sodium hydroxide on the polarographic behaviour of nickel (1·600 millimolar) in mono- and diethanolamine.

Curves 1 and 2 have been obtained in base solutions containing 0·1 M sodium hydroxide and 0·50 and 1·00 monoethanolamine respectively.

Curves 3 and 4 have been taken in base solutions containing 1·00 M sodium hydroxide and 0·50 and 1·00 M monoethanolamine respectively.

Curves 5, 6 and 7 have been taken in base solutions containing 1·00 M sodium hydroxide and 0·30, 0·65 and 1·00 M diethanolamine respectively.

Sensitivity: *s*/50.

The voltage lines preceding Curves 1 to 4 correspond to − 0·873 V *vs.* S.C.E., while those preceding Curves 5 to 7 correspond to − 0·973 V *vs.* S.C.E.

FIG. 3. Effect of sodium carbonate on the polarographic behaviour of nickel (1·600 millimolar) in monoethanolamine.

Curves 1 to 3 and 4 to 6 have been taken in 0·10 and 1·00 M sodium carbonate solutions using 0·30, 0·65 and 1·00 M monoethanolamine respectively.

Sensit vity: *s*/50.

The voltage line preceding each polarogram corresponds to − 0·773 V *vs.* S.C.E.

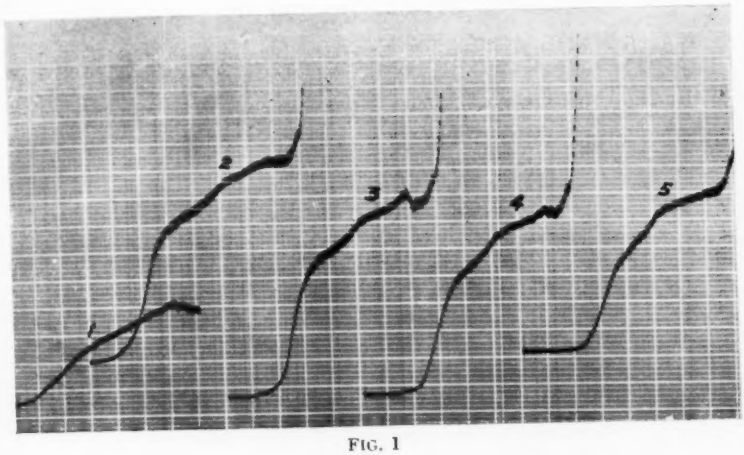

FIG. 1

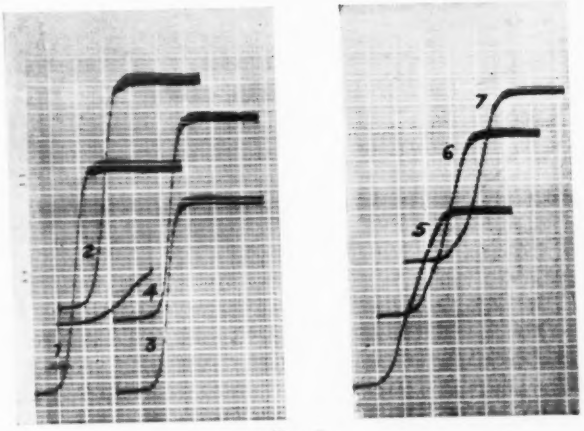

FIG. 2

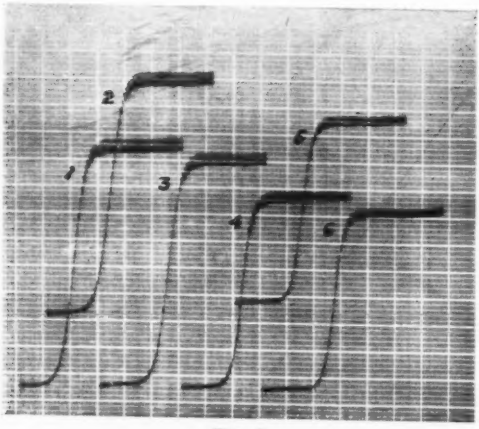

FIG. 3

POLAROGRAPHIC BEHAVIOUR OF METALS IN ETHANOLAMINES

Part IV. Cobalt (II)

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Introduction

In previous communications from this laboratory the polarographic behaviour of iron,[1] cadmium[2] and nickel[3] have been reported. In the present investigation a detailed study of the polarographic behaviour of cobalt (II) has been undertaken to elucidate the structure of the complexes that are formed and find out whether the polarographic waves of the complex metal ions produced under different conditions are suitable for the estimation of cobalt.

Experimental

The details of apparatus and experimental procedure employed have been described previously.[1] The capillary used had a drop-time of 5 seconds in 1 N potassium chloride solution and the value of m was 1·150 mg. per second. The polarograms were recorded at 30° ± 0·1° C.

Results

1. *Effect of pH*

In highly alkaline triethanolamine solutions, no wave has been obtained. As the pH is lowered to 11, the reduction wave appears but the diffusion current plateau is not flat due to the nearness of the final current rise. The best waves are obtained between pH 10–8 (Fig. 1). Even in these cases the diffusion current plateau is not sufficiently flat to enable the height of the wave to be accurately measured. Below pH 8, the shape of the wave is too poor to be of any practical use.

In diethanolamine solutions no wave is obtained at a pH of 13·5 while at ca. 12·7 ill-defined wave is obtained. Lowering of pH below 11·5 improves the shape of the wave further. In monoethanolamine solutions, on the other hand, fairly well-defined polarographic waves are obtained even at pH 13·5.

The results concerning the effect of pH on the half-wave potential and reversibility of the wave are given in Table I. These results indicate clearly that the waves are mostly irreversible in nature and that the extent of irreversibility varies with pH.

TABLE I

Effect of pH on the polarographic behaviour of cobalt in presence of ethanolamines

Concentration of cobalt: 1·440 millimolar; Concentration of gelatin: 0·005%; Concentration of amine: 0·10 M.

Amine used	pH	Half-wave potential $E_{\frac{1}{2}}$ *vs.* S.C.E. (Volt)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (Volt)
Monoethanolamine ..	6·5	−1·206	0·137
	9·2	−1·132	0·048
	11·0	−1·226	0·027
	12·7	−1·340	0·040
	13·5	−1·452	0·094
Diethanolamine	7·0	Ill-defined waves	
	7·8	−1·209	0·101
	9·0	−1·149	0·051
	10·7	−1·216	0·034
	12·7	−1·570	0·116
	13·5	Wave not formed	
Triethanolamine	7·0	Ill-defined waves	
	7·2	−1·293	0·075
	8·65	−1·244	0·066
	9·80	−1·279	0·044
	12·7	Wave not formed	
	13·5	do.	

2. *Effect of variation of the composition of the base electrolyte*

As the complex formation of cobalt takes place predominantly in the alkaline range, (i) sodium hydroxide, (ii) sodium carbonate, and (iii) ammonium chloride-ammonium hydroxide, have been employed in the base solutions.

(i) *Sodium hydroxide*.—In Table II are presented the results of the polarographic behaviour of ethanolamine complexes of cobalt in sodium hydroxide solutions. Gelatin (0·005%) was added to supress the maxima in solutions containing mono- and diethanolamines.

TABLE II

Effect of sodium hydroxide on the polarographic behaviour of cobalt in ethanolamines

Conc. of cobalt: 1·440 millimolar; Concentration of gelatin: 0·005%.

Amine used	Concentration of		Half-wave potential $E_{\frac{1}{2}}$ *vs.* S.C.E. (Volt)	$E_{\frac{1}{2}} - E_{\frac{1}{4}}$ (Volt)
	Amine (Molar)	Sodium hydroxide (Molar)		
Monoethanolamine	0·10	0·10	−1·340	0·040
	0·50	0·10	−1·355	0·061
	1·00	0·10	−1·371	0·059
	0·10	1·00	−1·452	0·094
	0·50	1·00	−1·497	0·070
	1·00	1·00	−1·507	0·057
Diethanolamine ..	0·10	0·10	−1·570	0·116
	0·50–1·00	0·10	Waves not formed	
	0·10–1·00	1·00	do.	
Triethanolamine ..	0·10–1·00	0·10–1·00	do.	

The results of Table II show that the irreversibility of reduction of diethanolamine complex is much greater than that of the monoethanolamine. It is surprising that irreversibility should diminish with increasing concentrations of monoethanolamine in 1 N sodium hydroxide.

(ii) *Sodium carbonate.*—Figure 2 gives some of the polarograms obtained with sodium carbonate solutions. It is clear from the figure that diethanolamine complexes give well-defined waves while the waves obtained in triethanolamine are complicated in nature. Curves in monoethanolamine are also well defined as in the case of diethanolamine. In triethanolamine there are two or three waves very close to each other. Even in the case of diethanolamine there is a slightly elongated bend before the diffusion current plateau. The results of analysis of the waves are given in Table III.

(iii) *Ammonium chloride and ammonium hydroxide.*—Figure 3 shows the polarograms obtained in presence of diethanolamine. Curves obtained in mono- and triethanolamines are similar in nature. Table IV indicates the results of the analysis of the waves. From the table it is clear that the waves are slightly irreversible in all the three amines.

TABLE III

Effect of sodium carbonate on the polarographic behaviour of cobalt in the presence of ethanolamines

Concentration of cobalt: 1·440 millimolar; Concentration of gelatin: 0·005%.

Amine used	Concentration of		Half-wave potential $E_{\frac{1}{2}}$ *vs.* S.C.E. (Volt)	$E_{\frac{1}{4}} - E_{\frac{1}{2}}$ (Volt)
	Amine (Molar)	Sodium carbonate (Molar)		
Monoethanolamine	0·10	0·10	−1·256	0·018
	0·50	0·10	−1·273	0·028
	1·00	0·10	−1·289	0·026
	0·10	1·00	−1·287	0·027
	0·50	1·00	−1·297	0·032
	1·00	1·00	−1·314	0·026
Diethanolamine ..	0·10	0·10	−1·298	0·066
	0·50	0·10	−1·374	0·109
			−1·58	
	1·00	0·10	−1·429	0·105
			−1·53	
	0·10	1·00	−1·333	0·070
	0·50	1·00	−1·437	0·122
	1·00	1·00	−1·508	0·128
Triethanolamine ..	Two or three poorly separated and ill-defined polagrams not amenable to analysis.			

TABLE IV

Effect of ammonium chloride (1 *M*)*—ammonium hydroxide* (1 *M*) *on the polarographic behaviour of cobalt in ethanolamines*

0·005% geatin used as maximum suppressor.

Amine used	Concentration of amine (Molar)	Half-wave potential $E_{\frac{1}{2}}$ *vs.* S.C.E. (Volt)	$E_{\frac{1}{4}} - E_{\frac{1}{2}}$ (Volt)
Monoethanolamine ..	0·10	−1·272	0·044
	0·50	−1·293	0·042
	1·00	−1·305	0·038
Diethanolamine ..	0·10	−1·279	0·053
	0·50	−1·300	0·048
	1·00	−1·311	0·040
Triethanolamine ..	0·10	−1·281	0·044
	0·50	−1·321	0·049
	1·00	−1·339	0·050

3. *Effect of concentration of cobalt on the diffusion current constant in presence of sodium hydroxide, sodium carbonate and ammonium chloride (1 M)—ammonium hydroxide (1 M)*

The results presented in Tables II and III indicate that the polarographic waves in sodium hydroxide solutions containing diethanolamine and triethanolamine are complicated and ill-defined and hence unsuited for the polarographic estimation of the metal. For a similar reason solutions containing sodium carbonate and triethanolamine are also not suitable. The effect of concentration of cobalt (II) on the diffusion current constant has been tested in base solutions containing monoethanolamine + sodium hydroxide, monoethanolamine + sodium carbonate, and diethanolamine + sodium carbonate where we get very well-defined waves. 0·005% or 0·025% gelatin has been included in the base solutions to eliminate the maximum. Due to the limited solubility of the complexes at low concentration of the amine, 1·00 M monoethanolamine and 0·5 M diethanolamine solutions have been used. Higher concentration of diethanolamine is not of much advantage as the diffusion current plateau is not well defined. As the addition of ethanolamines in base solution containing ammonium chloride-ammonium hydroxide does not have any practical advantage in the estimation of cobalt (II), these solutions have been omitted in testing the effect of concentration of cobalt (II) on the diffusion current constant. The results obtained are given in Table V, from which it is clear that these base solutions are suitable for the estimation of cobalt (II).

Discussion

(*i*) *Effect of pH*

The results given in Table I indicate that when the pH of the solution is decreased from 9 to about 7, the half-wave potential and the value of $E_{\frac{3}{4}}-E_{\frac{1}{4}}$ increase. The half-wave potential at pH 7 is $-1{\cdot}21$ V in mono- and diethanolamine and $-1{\cdot}29$ V in the case of triethanolamine. The above results indicate that the reduction step may be due to

$$Co\,(H_2O)_6^{++} \rightarrow Co.$$

This, however, does not seem consistent with the fact that the half-wave potential of hexacobaltous ion is $-1{\cdot}425$ V *vs.* S.C.E. A similar anomaly has also been noticed by Willis, Friend and Mellor,[4] who noticed a $E_{\frac{3}{4}}$ of $-1{\cdot}28$ V for the second wave of the Co^{++} complexes. This wave has been interpreted by the authors as due to the reduction of $Co\,(H_2O)_6^{++} \rightarrow Co$.

When the pH of the solution is increased to 9, the half-wave potential decreases and reduction process becomes more reversible in character. This

TABLE V

*Effect of concentration of cobalt on diffusion current constant**

Concentration of cobalt (Millimolar)	Diffusion current constant $\frac{i_d}{Cm^{\frac{2}{3}}t^{\frac{1}{6}}}$	Concentration of cobalt (Millimolar)	Diffusion current constant $\frac{i_d}{Cm^{\frac{2}{3}}t^{\frac{1}{6}}}$
(1) *B.S.:* 1·00 *M Moen*+0·10 *M NaOH*+0·005% *gelatin* $X = 1·381$ *at* $-1·50$ *V vs. S.C.E.*		(4) *B.S.:* 1·00 *M Moen*+1·00 *M* Na_2CO_3+0·025% *gelatin* $X=1·381$ *at* $-1·60$ *V vs. S.C.E.*	
1·440	3·04	1·440	2·55
7·200	3·05	7·200	2·57
14·400	3·05	14·40	2·48
(2) *B.S.:* 1·00 *M Moen*+1·00 *M NaOH*+0·005% *gelatin*		(5) *B.S.:* 0·50 *M Dien*+0·10 *M* Na_2CO_3+0·005% *gelatin* $X=1·360$ *at* $-1·75$ *V. vs. S.C.E.*	
1·440	2·86	1·440	2·98
7·200	2·85	7·200	2·95
14·400	2·84	14·40	2·87
(3) *B.S.:* 1·00 *M Moen*+0·10 *M* Na_2CO_3+0·025% *gelatin* $X=1·381$ *at* $-1·60$ *V. vs. S.C.E.*		(6) *B.S.:* 0·50 *M Dien*+1·0 *M* Na_2CO_3+0·005% *gelatin* $X=1·345$ *at* $-1·75$ *V vs. S.C.E.*	
1·440	3·12	1·440	2·38
7·200	3·06	7·200	2·36
		14·40	2·38

* *Abbreviations*—B.S.—Base solution; X—$m^{2/3}t^{1/6}$ in $mg^{2/3}$ $sec.^{-1/2}$; Moen—monoethanolamine; Dien—diethanolamine; Trien—triethanolamine.

indicates complex formation with the amine. At still higher pH values the hydroxyl group enters into the complex forming hydroxo-ethanolamino complex. The second increase in $E_{\frac{1}{2}}$ above pH 11 is perhaps due to the entry of OH^- group into the complex.

(ii) *Splitting of the polarographic wave*

Sodium carbonate solutions.—The reduction of Co (II) at the surface of the dropping mercury electrode is a stright two-electron step. Hence the splitting of the polarographic wave observed in triethanolamine solutions is due to two or three different species[2] in sluggish equilibrium. Similar explanation can be given for the elongated bend that appears before the diffusion current plateau in diethanolamine solutions. In monoethanolamine solutions, the splitting is practically absent. It is noteworthy that the tendency for splitting decreases progressively with the decrease in the number of ethanol groups in the amine.

Ammonium chloride-Ammonium hydroxide solutions.—The slight tendency for the splitting of the wave as indicated by a pressed-in bend before the diffusion current plateau is evident only when triethanolamine is used as the complexing agent.

(iii) *Irreversibility of the polarographic waves*

A perusal of the Tables I, II, III and IV indicates that the reduction of the ethanolamine complexes is essentially an irreversible process, excepting in the case of the monoethanolamine complex in presence of sodium carbonate solutions. In contrast to the behaviour of nickel[3] complexes, even some of the monoethanolamine complexes of cobalt are also irreversible and the extent of irreversibility increases with the number of ethanol groups in the amine. It is surprising that the hydroxomonoethanalo complex should be reduced irreversibly; perhaps, the reduction of the complex is activation controlled under these conditions.

(iv) *Nature of complex formation in sodium hydroxide solutions*

Application of the modified equations for irreversible processes[1] to the results presented in Table II indicates that one molecule of monoethanolamine is present in the complex. It is not possible to compute the number of hydroxyl groups in the complex as the reduction processes in 0·1 M and 1·0 M sodium hydroxide differ in irreversibility.

(v) *Nature of complex formation in sodium carbonate solutions*

Application of Lingane's equation for reversible processes[2] indicates the following formula for the complex:

$$Co\,(Moen)_2\,(CO_3)_1.$$

For reasons similar to those explained in the previous paper,[3] it has not been possible to calculate the thermodynamic constants of this complex.

In the case of diethanolamine, the reduction process is irreversible. From the equations for irreversible processes[1] it follows that two diethanolamine groups and one carbonate group enter the complex:

$$Co\,(Dien)_2\,(CO_3)_1.$$

(vi) *Nature of complex formation in presence of ammonium chloride and ammonium hydroxide*

From the results presented in Table IV it is clear that the ethanolamines enter into the ammonia complex. Applying the equations for irreversible processes,[1] it is found that one molecule of ethanolamine has entered into the complex.

In conclusion it may be stated that the polarographic studies of the cobalt complexes of ethanolamines have revealed the formation of the following complexes:

(1) $[Co\,(Moen)_1\,(OH)_x]^{2-x}$ (2) $Co\,(Moen)_2\,(CO_3)_1$
(3) $Co\,(Dien)_2\,(CO_3)_1$ (4) $Co\,(Moen)_1\,(NH_3)_y^{++}$
(5) $Co\,(Dien)_1\,(NH_3)_z^{++}$ (6) $Co\,(Trien)_1\,(NH_3)_a^{++}$.

It may also be pointed out that the reduction waves obtained in mono- and diethanolamines can be used for the estimation of cobalt.

SUMMARY

1. The polarographic behaviour of cobalt has been studied in ethanolamines employing the following electrolytes to alter the pH of the solutions: (i) Sodium acetate-acetic acid, (ii) Sodium carbonate, (iii) Sodium hydroxide, and (iv) Ammonium chloride-Ammonium hydroxide.

2. Studies of the effect of pH have indicated that in acidic solutions aquo-cobalt ion is reduced at the dropping mercury electrode. As the pH is increased to 9, the amine complex is formed, and when the pH is increased still further, hydroxyl group also enters into the complex.

3. The reduction of the ethanolamine complexes of cobalt at the dropping mercury electrode is essentially an irreversible process except in solutions containing sodium carbonate and monoethanolamine.

4. The foregoing studies indicate the formation of the following complexes of cobalt:—

(1) $[Co\,(Moen)_1\,(OH)_x]^{2-x}$ (2) $Co\,(Moen)_2\,(CO_3)_1$
(3) $Co\,(Dien)_2\,(CO_3)_1$ (4) $Co\,(Moen)_1\,(NH_3)_y^{++}$
(5) $Co\,(Dien)_1\,(NH_3)_z^{++}$ (6) $Co\,(Trien)_1\,(NH_3)_a^{++}$.

5. It has been indicated that the reduction waves of cobalt in mono- and diethanolamines can be used for the analytical estimation of the metal.

ACKNOWLEDGEMENT

The author expresses his sincere thanks to Prof. K. R. Krishnaswami and Dr. M. R. A. Rao for their helpful discussions.

REFERENCES

1. Subrahmanya, R. S. .. *Proc. Ind. Acad. Sci.*, 1956, **43 A**, 133.
2. ———— .. *Ibid.*, 1956, **43 A**, 383.
3. ———— .. *Ibid.*, 1957, **45 A**, 184.
4. Willis, J. B., Friend, J. A. and Mellor, D. P. *J. Amer. Chem. Soc.*, 1945, **67**, 1680.

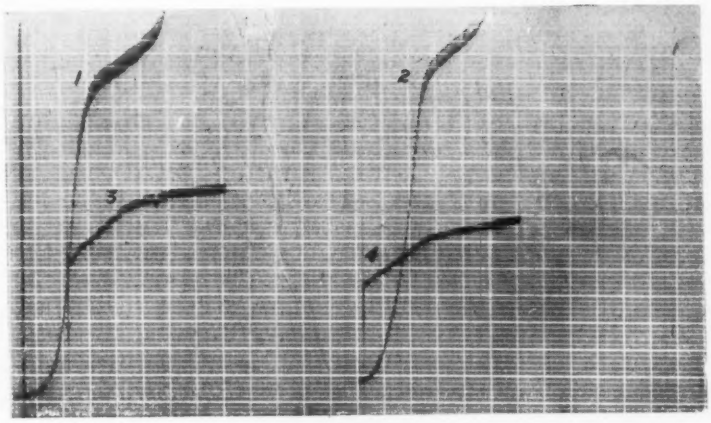

FIG. 1

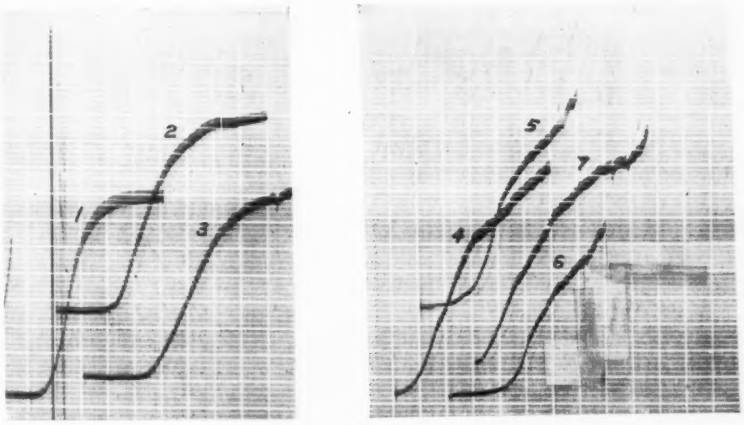

FIG. 2

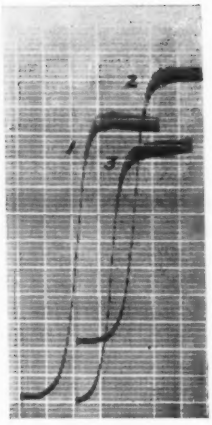

FIG. 3

Explanation of Plates

Fig. 1. Effect of pH on the polarographic behaviour of cobalt (1·440 millimolar) in triethanolamine.

Curves 1 and 2 have been taken at pH 9·8 and 8·65 respectively.

Curves 3 and 4 are for the reduction of Co^{+++}, $- Co^{++}$, Co^{+++} being formed by the oxygen present in the solution.

Sensitivity: *s*/30.

The voltage lines just preceding Curves 1 and 2 correspond to − 1·073 V *vs.* S.C.E. and those preceding Curves 3 and 4 correspond to 0·027 V *vs.* S.C.E.

Fig. 2. Effect of sodium carbonate (0·1 M) on the polarographic behaviour of cobalt (1·440 millimolar) and di- and triethanolamine.

Curves 1 to 3 are obtained in 0·10, 0·50 and 1·00 M diethanolamine respectively.

Curves 4 to 7 are obtained in 0·10, 0·50, 1·00 and 0·02 M triethanolamine respectively.

Sensitivity: *s*/50.

The voltage lines just preceding polarograms 1 to 3 correspond to − 1·073 V *vs.* S.C.E. and those preceding Curves 4 to 7 correspond to 1·273 V *vs.* S.C.E.

Fig. 3. Effect of ammonium chloride (1·0 M)—ammonium hydroxide (1·0 M) on the polarographic behaviour of cobalt (1·440 millimolar) in presence of diethanolamine.

Curves 1 to 3 are obtained employing 0·10, 0·50 and 1·00 M diethanolamine respectively.

Sensitivity: *s*/50.

The voltage lines just preceding the polarograms correspond to − 1·073, −1·073 and − 1·173 V *vs.* S.C.E.

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ERRATA

Vol. XLV, No. 2, Section A, February 1957

Page	*Line or Equation*	*For*	*Read*
107	6	$\frac{\partial u}{r\partial r}$	$\frac{\partial u}{r\partial \theta}$
108	3.3	$-K_0$	$+K_0$
110	4.1, 4.6	$-K_0$	$+K_0$
111	5.4, 5.5, 5.6, 5.7	$-K_0$	$+K_0$
111	5.9	Delete $-2K_0(1-c)$	
112	5.13 and last equation	$-K_0$	$+K_0$
112	5.11	Multiply the right-hand side, giving the values of a^2 and C_1^2 by $(3-2c)$	

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Bergmann and Stather . . . . . Z. Physiol. Chem., 1926, 152, 189.

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